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INFRARED SPECTRA OF CELLULOSE AND ITS DERIVATIVES

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Corrected and updated by the author for the American edition.

A systematic discussion of the infrared spectra of an important natural polymer — cellulose — and its derivatives. The infrared spectra of the main classes of cellulose derivatives are described and interpreted, as are those of model compounds such as mono-, di-, and trisaccharides. Considerable attention is given to technical problems involved in obtaining infrared spectra of fibrous cellulose materials, and the analytical possibilities of infrared spectroscopy. Spectra and tables are given in a 130-page appendix.

CONTENTS: Methods for Obtaining the Infrared Spectra of Cellulose and Related Materials: Investigation of unchanged fibrous material • The suspension method • The solid immersion media method • Production of thin fiber films without the use of an immersion medium • The production of infrared spectra of cellulose from alkaline aqueous solutions • The production of thin films of water-soluble compounds from their aqueous solutions • **Cellulose Model Compounds — Unmodified Cellulose:** Monosaccharides • Disaccharides • Polysaccharides • Cellulose from one-year-old plants • Cellulose from young wood shoots • Cellulose from wood of various ages • Samples of technical cellulose • **Hydrocellulose — Products of Partial Hydrolysis of Cellulose:** Cellulose regenerated after treatment with alkali of various concentrations • Cellulose subjected to grinding • Viscose fiber • The effect of hydrogen bonding on the structure of cellulose • Alkaline cellulose • Products of the partial hydrolysis of cellulose • **Cellulose Esters and Ethers:** Cellulose acetates, produced under homogeneous conditions of acetylation and partial hydrolysis • Cellulose acetates, produced under heterogeneous conditions of acetylation and partial hydrolysis • Comparison of spectral investigation data with the results of viscometric analyses of cellulose acetates • Acetylcellulose fibers with various acetyl group contents • Special features of the spectra of ethers and esters of cellulose • **Oxidation Products of Cellulose — Salts of Oxidation Products of Cellulose:** Monocarboxycellulose • Dialdehydocellulose • Dialdehydocellulose oxidized by nitrogen oxides • Dicarboxycellulose • Cellulose dialcohol • Salts of oxidation products of cellulose • Salts of cellulose oxidation products with inorganic cations • Salts of cellulose oxidation products with organic cations • **New Types of Cellulose Derivative:** Esters of cellulose with phosphorous-containing acids • Esters of cellulose with chlorinated fatty acids • Stable cellulose xanthate derivatives • Investigation of the products of thermal decomposition of cellulose methylxanthate • Cellulose compounds containing new functional groups • Graft copolymers of cellulose with poly-2-methyl-5-vinylpyridine • Graft copolymers of cellulose with carbon chain polymers, produced by initiating the graft polymerization with pentavalent vanadium compounds • Products of the ion-exchange of graft copolymers of cellulose and polyacrylhydroxamic acid with ions of Fe^{3+} and Cu^{2+} • **The Possibilities of the Infrared Spectroscopic Method for Investigation of the Properties of Cellulose and its Derivatives • Appendices.**

OF INTEREST TO: analytical, organic, physical, and inorganic chemists particularly concerned with treating cellulose, compounds related to cellulose (carbohydrates and polycarbohydrates), and other polymers, experimentally and under industrial conditions.

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A SPECTROSCOPIC METHOD FOR THE QUANTITATIVE DETERMINATION OF SMALL AMOUNTS OF RARE EARTH ELEMENTS WITHOUT THE USE OF STANDARDS

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The difficulties associated with the preparation of standards during the development and application of the various spectroscopic methods of quantitative analysis are generally known [1, 2]. These difficulties have become especially apparent in connection with the lack of the required amounts of pure preparations during the development of various methods of analysis of rare earth elements [3]. The method proposed in the present communication permits determination of small amounts of rare earth impurities in pure preparations of these elements without the use of standards. The concept behind the method involves the use of two comparison lines. This concept may be used for the development of methods for the analysis of other elements without the use of standards.

The ratio of the intensities of the line of the element being determined and the comparison line may be expressed in the form:

$$\frac{I_1}{I_c} = \frac{\alpha_1}{\alpha_c}\frac{N_1}{N_c}\frac{A_1}{A_c}e^{-\frac{E_1-E'_c}{kT}}\frac{h\nu_1}{h\nu_c}C^b, \qquad (1)$$

where, E_1 and E'_c are the excitation potentials of the analytical line and the comparison line, respectively; K is the Boltzman constant; T is the absolute temperature of the plasma; C is the content of the element in the sample; b is an exponent which is characteristic of the self-absorption of the line, and is equal to unity at small values of C; α_1 and α_c are coefficients which depend on the type of light source, the spectroscopic apparatus, the method by which the sample is introduced into the arc gap, processes originating during the transition of the sample into the vapor state, etc.; ν_1 and ν_c are the frequencies of the lines; h is Planck's constant; A_1 and A_c are transition probabilities; and N_1 and N_c are the total numbers of unexcited atoms of the given elements in the plasma of the arc.

Equation (1) is an analytical expression of a calibration graph. It is readily seen that, provided the content of the element does not change, the relative intensity of the line depends essentially on the temperature of the arc, except for the case where $E_1 = E_c$, a situation which is rarely encountered in actual practice. Changes in the current strength and in the values of the arc and discharge gaps lead to a substantial change in the arc temperature and, consequently, to a change in the relative intensity. This relationship is a difficultly controllable

TABLE 1

Dependence of the Terms of Equation (3) on Light Source Parameters

Parameters of the a/c arc	Thulium in erbium, λ_{Tu} 3362.6; λ'_{Er} 3369.2; λ''_{Er} 3368.0				Europium in gadolinium, λ_{Eu} 4435.5; λ'_{Gd} 4437.4; λ''_{Gd} 4431.4			
	$\lg \frac{I_{Tu}}{I'_{Er}}$	$A \lg \frac{I''_{Er}}{I'_{Er}}$	$\lg \frac{I_{Tu}}{I'_{Er}} + A \lg \frac{I''_{Er}}{I'_{Er}}$	B	$\lg \frac{I_{Eu}}{I'_{Gd}}$	$A \lg \frac{I''_{Gd}}{I'_{Gd}}$	$\lg \frac{I_{Eu}}{I'_{Gd}} + A \lg \frac{I''_{Gd}}{I'_{Gd}}$	B
l_1=5 a	0,05±0,02	0,18±0,02	0,23±0,05	−1,77±0,05	0,08±0,02	0,23±0,02	0,31±0,04	−1,69±0,04
l_2=14 a	0,09±0,02	0,13±0,02	0,22±0,04	−1,78±0,04	0,12±0,02	0,20±0,02	0,32±0,04	−1,68±0,04
l_1=3,5 mm	0,10±0,02	0,13±0,02	0,23±0,04	−1,77±0,04	0,14±0,02	0,18±0,02	0,32±0,04	−1,68±0,04
l_2=8 mm	0,21±0,02	0,04±0,01	0,25±0,03	−1,75±0,04	0,26±0,02	0,06±0,02	0,32±0,04	−1,68±0,04
d_1=0,5 mm	0,23±0,02	0,02±0,01	0,25±0,03	−1,75±0,04	0,28±0,02	0,05±0,02	0,35±0,04	−1,65±0,04
d_2=0,1 mm	0,09±0,01	0,15±0,02	0,24±0,03	−1,76±0,04	0,12±0,02	0,19±0,02	0,31±0,04	−1,69±0,04

Note: I_1 and I_2 are current strengths; l_1 and l_2 are intermolecular distances; d_1 and d_2 are activator discharge gaps.

TABLE 2

Comparison of Results of Analyses of Rare Earth Elements by the Method of This Article

Tm introduced into Er, %	Found by this method, %	Deviation	Eu introduced into Gd, %	Found by this method, %	Deviation
0,010	0,011	+0,001	0,010	0,009	−0,001
0,015	0,014	−0,001	0,015	0,014	−0,001
0,01	0,10	0	0,10	0,11	+0,01

source of error in the analysis, and it makes quantitative determination of the elements without the use of standards impossible.

In order to allow for this change in temperature, we take one additional comparison line, I''_c, belonging to the comparison element. Then:

$$\frac{I''_c}{I'_c} = \frac{A''_c}{A'_c} \cdot e^{-\frac{F''_c - F'_c}{kT}}. \qquad (2)$$

Eliminating the temperature from Eq. (1) and (2), we obtain:

$$\lg C = \lg \frac{I_1}{I'_c} + A \lg \frac{I''_c}{I'_c} + B, \qquad (3)$$

where

$$A = -\frac{E_1 - E'_c}{E''_c - E'_c},$$

$$B = A \lg \frac{A''_c}{A'_c} - \lg \left(\frac{\sigma_1}{\alpha_c} \frac{N_1}{N_c} \frac{A_1}{A_c} \frac{h\nu_1}{h\nu_c} \right).$$

The right side of this equation does not depend on arc temperature. Consequently, by determining only once the coefficients A and B for a given apparatus, the parameters of which remain constant, subsequent determinations of the elements are possible by means of Eq. (3) without the use of standards. The coefficients A

and B are determined by solution of a system of two equations for two values of the concentration C. The problem of the present investigation consisted of the experimental proof that the right side of Eq. (3) is independent of changes in the parameters determining the operating regime of the light source.

Table 1 presents the experimental data obtained during the determination of small amounts of thulium in erbium and of europium in gadolinium (the apparatus and the preparation of the samples for analysis were similar to those described in [3]). It is apparent that the first two terms of the right side of Eq. (3) each separately underwent substantial changes with a change from one set of arc conditions to another, while the sum of these terms and the coefficient B remained constant within the limits of error of the measurements. This circumstance permits use of the values of the coefficients for further analysis without the use of standards. Investigation showed that the root mean square error of a single determination by the present method of small amounts of rare earth elements present as impurities in pure preparations of these elements is ± 15-20%.

Table 2 presents for comparison the results of determinations of thulium in erbium and of europium in gadolinium by the method of the present article. It is apparent from an inspection of the data presented that the results of the analyses agree with the amounts introduced within the above limits of error.

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THE INTERACTION OF N-BENZOYL(O-BENZOYLPHENYLALANYL-C^{14})-SERINE WITH ALBUMINS

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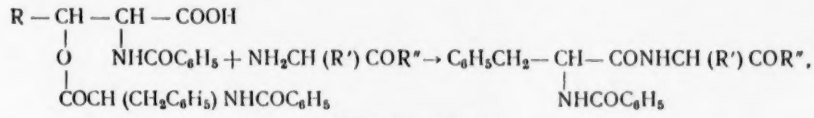
Recent investigations have established that synthesis of albumin outside organisms can be accomplished by various methods [1], including transfer of amino acid and peptide residues from intermediate energy-rich compounds. In particular, Fruton and co-workers [2] found that the synthesis of the peptide chain in albumin can be carried out by means of transamidation. The interaction of glycyl-L-tyrosine-C^{14} amide with insulin in the presence of a cathepsin resulted in the addition of glycyl-L-tyrosine to the glycine amino group in the "A" chain. We have recently shown [3] that O-peptides of serine, threonine, and glycolic acid, particularly N-benzoyl(O-benzoylphenylalanyl)serine*, react very readily with esters of amino acids and peptides under the influence of chymotrypsin with the formation of esters of optically active peptides:



where R = H, CH_3
R″ = OC_2H_5 or a peptide ester residue.

It seemed to us to be not without interest to apply a radioisotope method in an effort to confirm the possibility of transferring amino acid residues from O-peptides of β-hydroxyamino acids to albumin. With this aim in view, N-benzoyl(O-benzoylphenylalanyl-C^{14}) serine was synthesized and was reacted with insulin and with blood serum albumin under conditions previously developed for the synthesis of optically active N-peptides from O-peptides of β-hydroxyamino acids. Upon completion of the reaction, the albumin was precipitated with trichloroacetic acid (TCA), washed with alcohol and with ether, and dried. The radioactivity of the albumin was determined with an end-window counter. In order to remove O-peptide possibly adsorbed on the albumin, the preparation was treated with a base and precipitated with TCA, and its activity was again determined. At the same time, control experiments were carried out without an enzyme and with chymotrypsin previously inactivated by boiling. The degree of transfer of benzoylphenylalanine-C^{14} was calculated in μ-equivalents per gram of albumin per hour and in μ-equivalents per μ-equivalent of albumin (Tables 1 and 2). The experimental data are summarized in Tables 1, 2, and 3. A comparison of the results obtained with insulin and with blood serum albumin in the presence and in the absence of chymotrypsin shows that transfer of benzoylphenylalanine-C^{14} from the O-peptide to the albumin is promoted by the enzyme. The degree of transfer depends on the mole ratio of O-peptide (donor) to albumin (acceptor), and was different for each albumin. Thus, for insulin the degree of transfer increases with an increase in the mole ratio of donor to acceptor, while for blood serum albumin, the degree of transfer was greatest at a mole ratio of 5 : 1.

*We shall refer to this as O-peptide in the future.

TABLE 1

Interaction of N-Benzoyl(O-benzoylphenylalanyl-C^{14})serine with Blood Serum Albumin

Expt. No.	Component mole ratio, O—N-peptide / albumin	O—N-peptide, mg	Albumin, mg	Initial activity in test, imp / min	Amount of labeling: imp / min per 5 mg albumin••• after TCA	after 1 N NaOH••	μ equiv peptide: per g of albumin per hr	per μ-equiv of albumin•••	Enzyme	Notes
1	1 : 1	0,4	60	10800	5•	0••	0	0	—	
2	2,5 : 1	1	60	27000	173	112	1,8	0,12	Chymotrypsin	
3		1	60	27000	110	62	1,0	0,06	No enzyme	
4		1	27	27000	477	162	2,6	0,168	Chymotrypsin	After 3 hr in 1 N NaOH, 140 imp / min
5		1	30	27000	487	173	2,77	0,17	"	
6	5 : 1	1	30	27000	81	63	1,04	0,06	"	
7		1	30	27000	160	56	0,90	0,06	"	After 1 hr in 1 N NaOH, 54 imp / min
8		1	30	27000	57	15	0,25	0,015	—	
9		1	30	27000	123	26	0,43	0,03	—	
12	0 : 1	1	13,5	27000	60	23	0,4	0,03	Chymotrypsin	Incubation time, 22 hr
		1	13,5	27000	142	75	1,25	0,08	"	
		1	13,5	27000	43	32	0,53	0,035	—	
10	20 : 1	10	78	270000	17	11	0,19	0,016	Chymotrypsin	
11		10	78	270000	22	13	0,2	0,016	"	
13		20	25	540000	50	4	0,06	0,003	—	Vol. of reaction mixture, 25 ml
14	100 : 1	20	25	54000	60	12	0,19	0,012	Chymotrypsin	

•Arithmetic average of two measurements.

••Arithmetic average of four measurements.

•••The activity cited takes background into account.

••••Mol. wt. of albumin 65,000.

In order to answer the question of whether the observed radioactivity was due to the direct addition of N-benzoyl(O-benzoylphenylalanyl)serine to the albumin rather than to enzyme-promoted transfer of benzoylphenylalanine, the serum albumin obtained after incubation and reprecipitation with alkali was again treated with 1 N base and allowed to stand for 1 or 3 hr. The activity was then again determined (Table 1, Expts. 5 and 6); it had changed only insignificantly. Moreover, according to the data of M. M. Botvinik and S. M. Avaeva [3], O-peptides are hydrolyzed completely under these conditions; therefore, the albumin should have lost activity. Finally, special experiments on the incubation of albumins with benzoylphenylalanine-C^{14} showed that the latter is not added to the albumin (see Table 3). These negative experiments confirm that the addition of the label occurs through the transfer of the aminoacyl residue from the O-peptide, and not by direct incorporation of benzoylphenylalanine-C^{14}; the latter could be formed by hydrolysis of the O-peptide.

The stability of the preparations with respect to bases suggests that the addition proceeds through the formation of stable, apparently peptide bonds. This assumption requires further investigation. Some confirmation is provided by the results obtained by Fruton [2].

EXPERIMENTAL

Synthesis of N-benzoyl(O-benzoylphenylalanyl-C^{14})serine. Phenylalanine-C^{14} was prepared from glycine-C^{14} (in the carboxyl) by the azlactone method [4]. The m.p. was 270-272°; the literature reports 271-273° [4]. The benzoylphenylalanine-C^{14} had an m.p. of 184-185°; the literature reports an m.p. of 186° [5]. The N-benzoyl-(O-benzoylphenylalanyl-C^{14})serine had an m.p. of 168°; the literature reports an m.p. of 171° [6]. The yield was 21.6% calculated on the original glycine. It was prepared by the method of M. M. Botvinik and S. M. Avaeva [6].

TABLE 2

Interaction of N-Benzoyl(O-benzoylphenylanalyl-C^{14})serine with Insulin

Expt. No.	Component mole ratio, O-N-peptide / albumin	O-N-peptide, mg	Albumin, mg	Initial activity in test, imp / min	Amount of labeling: imp / min per 5 mg albumin*** after TCA*	after 0.1 N NaOH**	Amount of labeling: μ-equiv. peptide per g of albumin per hr	per μ-equiv of albumin****	Enzyme
15		1	20	21975	71	61	1,2	0,007	Chymotrypsin
16	0,65 : 1	1	20	39222	82	75	0,84	0,005	"
17		1	20	21975	41	11	0,22	0,0012	No enzyme
18		1	20	39222	91	43	0,48	0,0027	" "
19		3	20	53280	743	168	4,1	0,024	Chymotrypsin
20		3	20	65925	231	165	3,26	0,02	"
21		3	20	65925	200	150	3,0	0,018	"
22		3	20	65925	230	157	3,14	0,019	"
23	2 : 1	3	20	86310	244	162	2,44	0,014	"
24		3	20	65925	128	31	0,62	0,0037	No enzyme
25		3	20	117666	250	69	0,74	0,0044	" "
26		3	20	53280	391	39	0,95	0,006	" "
27		3	20	86310	27	22	0,34	0,0019	RNC
28		3	20	86310	25	23	0,34	0,0019	"
29		3	20	86310	46	40	0,59	0,0033	Chymotrypsin inactivated
30		3	20	86310	47	37	0,54	0,003	by boiling
31		5	20	196110	454	264	2,9	0,017	Chymotrypsin
32		5	20	196110	438	246	2,8	0,016	"
33	3,3 : 1	5	20	196110	410	55	0,60	0,0035	No enzyme
34	10 : 1	15	20	479550	1130	421	5,7	0,033	Chymotrypsin
35		15	20	479550	1770	61	0,82	0,0047	No enzyme
36		30	20	959100	2538	669	9,05	0,052	Chymotrypsin
37		30	20	959100	2602	73	0,99	0,0057	No enzyme
38		30	20	800000	935	796	10,3	0,06	Chymotrypsin

*Arithmetic average of two measurements.

**Arithmetic average of four measurements.

***The activity cited takes background into account.

****Mol. wt. of insulin 6000.

Equivalent weight: found, 440 (by titration), 479 (by saponification of the ester bond); calculated for $C_{26}H_{24}O_6N_2$, 460. The specific activity was 0.105 mC per g. Crystalline insulin and crystalline blood serum albumin were used in the investigations. Both preparations were electrophoretically homogeneous.

Interaction of O-peptide with albumins. A weighed sample of the albumin was dissolved in $^1/_{15}$ M phosphate buffer (pH 8.2), and the required amount (see Table 1) of O-peptide dissolved in the same buffer was added. The pH of the medium was brought to 8-8.5 by the addition of 0.1 N NaOH, and the crystalline chymotrypsin was then introduced (0.2-0.25 mg per experiment). The total volume of the reaction mixture was 2.5-3 ml, and the mixture was incubated in a thermostat at 23-24° for 1 hr. The albumin was then precipitated with TCA (final concentration 5%). The precipitate was centrifuged, washed five times with 5% TCA, three times with a mixture of alcohol and ether (1 : 3), and twice with ether, and then dried. Samples for the determination of radioactivity by means of the end-window counter were prepared on metal plates from 5 mg of the dried, incubated albumin. Measurement of the activity was carried out with counters of differing efficiencies, which explains the variation in specific and initial activity of the O-peptide in the different experiments. The root mean square deviation in the radioactivity measurements on different samples did not exceed 10%.

TABLE 3

Interaction of Albumins with Benzoylphenylalanine-C^{14}

Expt. No.	Albumin	Benzoyl-phenyl-alanine, mg	Albumin, mg	Initial activity, imp / min	Imp / min per 5 mg albumin		Enzyme
					after TCA	after 0.1 N NaOH	
39	Serum albumin	0.6	30	16200	3	0	Chymotrypsin
40		0.6	30	16200	7	4	"
41		1.7	20	59755	5	2	"
42	Insulin	1.7	20	59755	14	9	"

Purification of the incubated albumin by solution in alkali. The albumin preparations obtained after incubation were dissolved in 0.1 N NaOH (in 1 N NaOH in the case of blood serum albumin), and reprecipitated by the addition of 10% TCA. The precipitate was centrifuged, washed, dried, and the activity measurements were then carried out as described above. The results of the experiments are presented in Tables 1, 2, and 3.

Interaction of benzoylphenylalanine-C^{14} with albumins. The experiments were carried out in a manner similar to that described above, except that labeled benzoylphenylalanine was used in place of O-peptide (see Table 3).

Thus, this investigation has shown that under the influence of chymotrypsin, N-benzoyl(O-benzoylphenylalanyl-C^{14})serine reacts with insulin and blood serum albumin with transfer of the benzoylphenylalanine residue to the albumin.

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SYNTHESIS OF TRANS-1-HYDROXY-1-ACETOXYACETYL-6-ACETOXY-4,5-(4'-METHOXYBENZO)HYDRINDANE – AN ANALOG OF CORTICOID HORMONES

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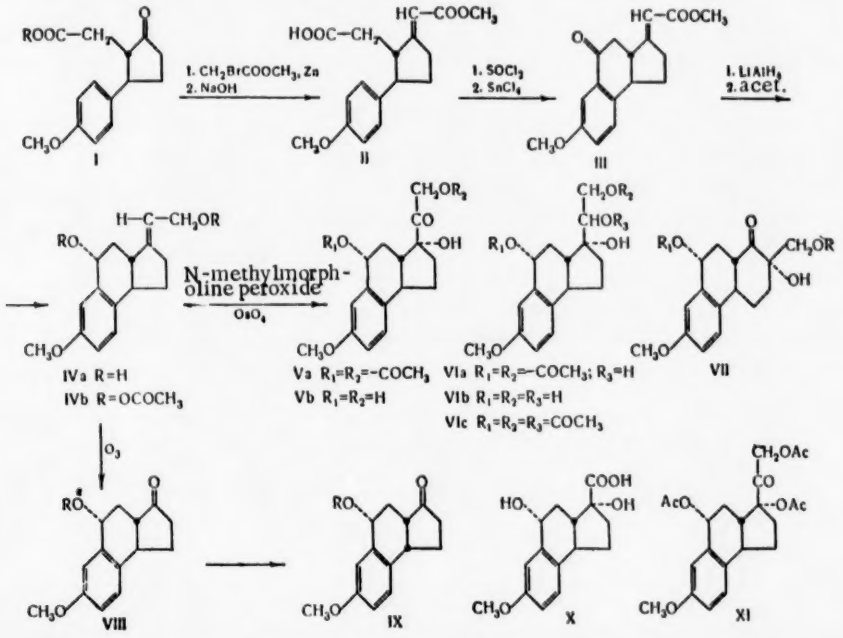
With the aim of preparing tricyclic analogs of steroid hormones containing a dihydroxyacetone or a glyceryl side chain in addition to other functional groups, we followed the synthesis route represented by Scheme 1. The relative simplicity of the preparation of the original trans-acid (I, R = H) [1], which contains two rings and a carboxymethylene chain useful in forming the third ring, makes possible the synthesis of polycyclic systems with a trans-attached ring by a short synthesis route. Replacement of the carbonyl group by a carbomethoxymethylene group permits cyclization of acid (II) with a yield of 75% and subsequent preparation of the compound containing a dihydroxyacetone or a glyceryl side chain; cyclization of the trans-keto acid (I, R = H) and its derivatives (ethylene ketal, acetoxy and methoxy derivatives) led to the formation of lactones [2, 3].



The methyl ester of trans-2-carboxymethyl-3-(p-anisyl)cyclopentyliden-1-acetic acid (II) was prepared by a Reformatskii reaction in which the keto ester (I, R = CH_3) was condensed with methyl bromoacetate and

subsequent dehydration; the yield was 35-37%. The exocyclic position of the double bond in acid (II) was confirmed by ultraviolet spectroscopy; the spectrum contained maxima at 226 and 275 mμ. Acid (II) was isolated as a single geometric isomer with an m.p. of 125-126°, and it apparently had the trans-configuration,• since the cis-isomer should experience considerable steric hindrance.

Found %: C 67.19; H 6.78
$C_{17}H_{20}O_5$. Calculated %: C 67.09; H 6.62

Cyclization of acid (II) by the Friedel-Crafts method gave the methyl ester of trans-6-keto-4,5-(4'-methoxybenzo)hydrindyliden-1-acetic acid (III) with an m.p. of 168-169°, λ_{max} 226 mμ (log ε 4.26; 3.7). The yield was 75-78%.

Found %: C 71.32; H 6.25
$C_{17}H_{18}O_4$. Calculated %: C 71.31; H 6.34

The 2,4-dinitrophenylhydrazone melted at 285° with decomposition.

Found %: N 12.01
$C_{23}H_{22}O_7N_4$. Calculated %: N 12.18

The carbomethoxymethylene chain was converted to a dihydroxyacetone or glyceryl chain by the method described by Hogg and co-workers [5], which includes three stages: reduction with lithium aluminum hydride, acetylation of the resulting alcohol, and, finally, oxidation of the $\Delta^{17,20}$-21-acyloxysteroids by means of N-methylmorpholine peroxide in the presence of a catalytic amount of osmium tetroxide.

Reduction of keto ester (III) with lithium aluminum hydride gave trans-6-hydroxy-4,5-(4'-methoxybenzo)-hydrindyliden-1-ethyl alcohol (IVa) with an m.p. of 141-141.5°. The yield was 78%.

Found %: C 73.81; H 7.84
$C_{16}H_{20}O_3$. Calculated %: C 73.82; H 7.74

Acetylation of (IVa) gave the diacetate (IVb) with an m.p. of 67.5-68.5°; the yield was 70-75%.

Found %: C 69.90; H 7.19
$C_{20}H_{24}O_5$. Calculated %: C 69.75; H 7.03

As we have previously reported [6], reduction of the carbonyl group in compound III to an alcohol group proceeded stereospecifically with the formation of a hydroxyl which apparently occupied the equitorial position (α), since in contrast to steroids, the β-region is not screened by angular methyl groups, and, therefore, approach of the reagent from the β-region can lead to the formation of the thermodynamically more stable hydroxyl group.

Oxidation of compound (IVb) by means of N-methylmorpholine peroxide led to a mixture of substances, chromatographic separation of which on silica gel yielded trans-1-hydroxyacetoxyacetyl-6-acetoxy-4,5-(4'-methoxybenzo)hydrindane (Va, $R_1 = R_2 = COCH_3$) with an m.p. of 120-121° (30% yield, R_f 0.03) and trans-1-hydroxy-1-(α-hydroxy-β-acetoxyethyl)-6-acetoxy-4,5-(4-methoxybenzo)hydrindane (VIa, $R_1 = R_2 = COCH_3$, R_3 = H) in the form of an oil (30% yield, R_f 0.03).•• The structures of these substances were established as follows. Substance(Va) gave an intense color with triphenyltetrazoline chloride, and its infrared spectrum exhibited absorption bands at 1730 and 3500 cm^{-1}, which are characteristic of CO- and OH- groups.

Found %: C 63.52; H 6.30
$C_{20}H_{24}O_7$. Calculated %: C 63.82; H 6.43

Saponification gave a compound (Vb, $R_1 = R_2$ = H) with an m.p. of 194-196°; the compound contained one carbonyl group (1708 cm^{-1}).

Found %: C 65.96; H 6.90
$C_{16}H_{20}O_5$. Calculated %: C 65.73; H 6.90.

•The stereoselectivity (formation of the trans-isomer) of this type of reaction was demonstrated by Linstead [4].
••Separation of the substances described in the present paper by paper chromatography was carried out in a benzene-formamide mixture. The chromatograms were developed with a saturated solution of antimonous chloride in chloroform.

However, compound (Va) formed neither a semicarbazone nor a 2,4-dinitrophenylhydrazone. Periodic acid oxidized it to an acid (X) with an m.p. of 148-150°, which confirms the presence of a dihydroxyacetone chain. This substance (Va) was not acetylated by acetic anhydride in pyridine under the usual conditions. By acetylation under conditions such that acetylation of the hydroxyl group in the 17 α-position could occur (in the presence of p-toluenesulfonic acid as a catalyst), the triacetate (XI) was obtained; m.p. 169-169.5°, R_f = 0.93.

Found %: C 63.07; H 6.39
$C_{22}H_{26}O_8$. Calculated %: C 63.14; H 6.27

By analogy with the oxidation of $\Delta^{17,20}$-21-acyloxysteroids with N-methylmorpholine peroxide and also owing to the behavior of Va during acetylation of the tertiary hydroxyl, we assume that in our case the relative positions of the groups at C_1 are analogous to the arrangement at C_{17} in corticosteroids.

When the reaction product from the oxidation with N-methylmorpholine peroxide was chromatographed over aluminum oxide, instead of substance Va with an m.p. of 120°, a substance with an m.p. of 177-178° was obtained. The yield was 25%. Evidently, rearrangement of (Va) to compound (VII) (found %: C 64.01; H 6.57; $C_{20}H_{24}O_7$) takes place over aluminum oxide; the infrared spectrum of this compound had absorption bands at 1735 cm^{-1} and 3500 cm^{-1}, which is characteristic of CO- and OH- groups. Substance (VII) gave a 2,4-dinitrophenylhydrazone with an m.p. of 250-252°, and it did not color a solution of triphenyltetrazoline chloride.

Hydroxylation of (IVb) by means of osmium tetroxide gave a substance (VIb, $R_1 = R_2 = R_3 = H$) with an m.p. of 193.5-194.5°, R_f = 0.8.

Found %: C 65.63; H 7.66
$C_{16}H_{22}O_5$. Calculated %: C 65.29; H 7.54

The triacetate (VIc, $R_1 = R_2 = R_3 = COCH_3$) had an m.p. of 121-122°, R_f = 0.8.

Found %: C 63.09; H 6.68
$C_{22}H_{28}O_8$. Calculated %: C 62.85; H 6.71

A mixture of the latter with Va melted with depression of the melting point, and its infrared spectrum had absorption bands at 1732 and 3450 cm^{-1}, which is characteristic of CO- and OH- groups. Acetylation of substance (VIa) also gave a triacetate with an m.p. of 121-122°, which did not cause depression of the melting point when mixed with triacetate (VIc).

In the preparation of (Va), we started with the trans-keto acid (I). During the course of the synthesis described above, it is possible for isomerization to occur with the formation of the more stable cis-system from the trans-hydrindane system. In order to establish the configuration of the addition of the five-membered ring to the six-membered ring, (IVb) was subjected to ozonation. The reaction resulted in the formation of acetoxyketone (VIII) with an m.p. of 153.5-154.5°, R_f = 0.9. The yield was 57%.

Found %: C 69.83; H 6.77
$C_{16}H_{18}O_4$. Calculated %: C 70.04; H 6.61

The acetoxyketone was subjected to alkaline isomerization with the aim of obtaining the stable isomer. The reaction yielded acetoxyketone (IX) with an m.p. of 80.5-81.5° (found %: C 69.64 ; H 6.72). Since the stable configuration of the hydrindane system is the cis-configuration, compound (IV) and all precursor compounds had the labile trans-configuration peculiar to steroid hormones.

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EXTRACTION WITH TWO COMPLEXING AGENTS

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An improvement in the extractability of metal chelate compounds has been observed, in a number of cases, upon the addition of certain polar substances (alcohols, amines, etc.) [1-3], and of substances having a structure approximating that of the complexing agent [1]; further, improvement has also been noted when a sufficient excess of the particular complexing agent is present [4, 5]. It has been reported [1] that sometimes the presence of very small amounts of these additives is sufficient to bring about a sharp increase in the distribution coefficient. Such phenomena have been explained by hydrophobization of the chelate molecules with a simultaneous increase in oleophilic nature owing to replacement of the coordinated water molecules by molecules of the added organic material [1, 3] and also owing to screening of parts of the chelate molecules with increased charge density.

We have investigated the effect of a second complexing agent on the extractability of chelate complexes under conditions where one or the other of two complexing agents, taken individually, is insufficient for extraction of the given metal. The following complexing agents were used: pyridine (I), 3, 5-dimethylpyrazole (II), 4,5-dimethylimidazole (III), ethylenediamine (IV), 2,2'-bipyridyl (V), 1, 10-phenanthroline (VI), 5,5'-dimethyl-3,3'-bipyrazyl (VII), 1-(2-pyridyl)-3,5-dimethylpyrazole (VIII), pentachlorophenol (IX), 8-hydroxyquinoline (X), 2-methyl-8-hydroxyquinoline (XI), 5-methyl-8-hydroxyquinoline (XII), 5,7-dichloro-8-hydroxyquinoline (XIII), N-nitrosophenylhydroxylamine (XIV), N-benzoyl-p-tolylhydroxylamine (XV), acetylacetone (XVI), 8-p-toluenesulfonylaminoquinoline (XVII), sodium diethyldithiocarbamate (XVIII), 2,2'-dihydroxyazobenzene (XIX), 4-nitro-2,2'-dihydroxy-5'-methylazobenzene (XX), 5-nitro-2,2'-dihydroxy-5'-methylazobenzene (XXI), 4-nitro-2,2'-dihydroxy-4'-methyl-5'-isopropylazobenzene (XXII), 5-chloro-2,2'-dihydroxybenzene-(1-azo-1)-naphthalene (XXIII), 2-hydroxy-4-methyl-3,5-diisopropylazobenzene-2'-arsonic acid (XXIV), benzene-(1-azo-1')-2'-naphthol-2-arsonic acid (XXV), 2-naphthol-(1-azo-1')-4'-methylbenzene-2'-sulfonic acid (XXVI), 2-naphthol-(1-azo-1')-4'-nitrobenzene-2'-sulfonic acid (XXVII), 2-hydroxy-(1-azo-2')-naphthalene-1'-sulfonic acid (XXVIII), 2-hydroxy-(1-azo-1')-naphthalene-8'-sulfonic acid (XXIX), and 2-hydroxy-(1-azo-1')-naphthalene-2'-sulfonic acid (XXX).

For each of the cations investigated, the change in color of the organic phase during extraction was studied in the following systems over the pH interval of 1 to 13: 1) reagent 1• and 2; 2) reagent 1 + cation; 3) reagent 1 + reagent 2; 4) reagent 1 + reagent 2 + cation; 5) reagent 2 + cation; 6) reagent 2. In cases where in systems of the type of 4 the color differed sharply from the color of the remaining control systems, the investigation was carried out in greater detail.

Chloroform was used as the extractant with all systems. Carbon tetrachloride, isoamyl alcohol, and dibutyl ether were also used in certain cases.

In the majority of cases, color effects were noted for copper, cobalt, and nickel with combinations of reagents of Types I-VIII with reagents of Types XIX-XXX; these effects were due to the simultaneous presence

• The Arabic numerals distinguish two reagents used in the combinations described in the latter part of the article—Translator.

of two complexing agents. This phenomenon was somewhat less characteristic of zinc, cadmium, lead, mercury (II), silver, and thallium (I).

In certain cases, combination of reagents of Types XXVIII with reagents of Types XIX-XXV caused these effects during the extraction of beryllium, magnesium, calcium, strontium, manganese (II), scandium, yttrium, lanthanum, and trivalent rare earth elements. Color effects were more rarely observed with barium, aluminum, zirconium, hafnium, thorium, and uranium (VI). It was sometimes possible to find conditions under which the selectivity of the reaction was high when extraction was carried out in the presence of two reagents. Certain interesting cases of selectivity of this phenomenon are cited below.

Copper (II): Reagents of the type of I-VIII in combination with IX at a pH of 6.0-8.0 (especially the combination of VIII with IX) and also in combination with reagents XXVI-XXX (especially in combination with XXX at a pH of 8-13 in the presence of very many of the different cations.

Zinc: Reagents XX-XXII in combination with III at a pH of 4.5-7.5 in the presence of cadmium, mercury (I, II), and lead.

Cadmium: Reagents II-XXII in combination with V-VIII at a pH of 8-11 in the presence of zinc, lead, and mercury.

Calcium: Reagent XVII in combination with XX or XXII at a pH of 8-13 (especially during extraction with carbon tetrachloride) in the presence of beryllium, strontium, barium, and small amounts of magnesium.

Scandium: Reagents X-XIII in combination with XIX-XXIII at a pH of 7.5-12 in the presence of aluminum yttrium, lanthanum, the rare earths, thorium, uranium, zirconium, and others.

Yttrium, lanthanum, and the rare earth elements (trivalent): Reagents XIV, XVI, and XVIII in combination with XIX-XXII at a pH of 8-12 and combinations of XIV with XXIV and XXV at a pH of 12-13 in the presence of aluminum, scandium, thorium, zirconium, uranium, and others.

Thorium: Reagents XX-XXII in combination with XV at a pH of 5.0-7.5 in the presence of aluminum, scandium, yttrium, the rare earth elements, zirconium, uranium, and others.

The appearance of unusual colors during extractions in which two complexing agents are used can most probably be explained by extraction of neutral, mixed chelate complexes. Some cases of extraction of mixed chelate compounds have been mentioned in the literature [6-11]. However, the possibility that simple or mixed chelate formation was, in our cases, associated with the effects mentioned in the present article cannot be excluded.

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OXYGEN-INITIATED HETEROGENEOUS CATALYTIC POLYMERIZATION OF ETHYLENE IN THE PRESENCE OF HYDROGEN

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We have established that the hydrogenation of ethylene at atmospheric pressure and a temperature of 100° in the presence of a cobalt-clay catalyst (which is a catalyst for the hydropolymerization of olefins under the influence of carbon monoxide [1]) is accompanied by polymerization reactions leading to the formation of gaseous dimer and liquid hydrocarbons. This observation is unexpected, since up to the present time, polymerization of ethylene has not been observed during hydrogenation of ethylene over this same catalyst but at a somewhat higher temperature, provided, of course, that the feed gas does not contain carbon monoxide in even insignificant amounts [2]. A more detailed investigation showed that the polymerization of ethylene in the presence of hydrogen at 100° is not initiated by carbon monoxide, but by oxygen, which is present as a slight impurity in the feed-gas mixture. In contrast to the hydropolymerization of ethylene (under the influence of small amounts of carbon monoxide), which is accelerated by an increase in temperature over the interval of 120 to 200°, the oxygen-initiated reaction, on the contrary, is slowed down by an increase in temperature over this same interval, and it proceeds most vigorously at 100-120°. The reaction is also inhibited by an increase in the concentration of oxygen in the feed-gas mixture over the interval studied (up to 2%), and does not occur at all in the absence of oxygen. The reaction does not take place with ethylene alone in the absence of hydrogen. The present paper presents a brief description of some results obtained in an investigation of this new type of heterogeneously catalyzed polymerization of ethylene in the presence of hydrogen, a reaction which is initiated by small amounts of oxygen.

The apparatus, the composition and method of preparing the catalyst, and the experimental method remained as previously described [1, 2]. Each portion of catalyst (18 g) contained 5 g of metallic cobalt. The volume of catalyst charged to the reaction tube (which was a 10-mm diameter Pyrex tube) was 25 ml. The experiments were carried out in a flow system at a feed-gas space rate of about 100 hours^{-1}. The ethylene was prepared by dehydration of ethyl alcohol over aluminum oxide, or, when complete exclusion of carbon monoxide from the feed gas was required, the ethylene was prepared by debromination of ethylene bromide by zinc dust in an alcohol medium [3]. Electrolytic hydrogen was used in all cases. The ethylene and hydrogen from which the feed-gas mixture was prepared were almost completely freed of oxygen (less than 0.1% O_2) by passing them separately over reduced copper at 170°. The reaction products were collected in two receivers; the first receiver was at room temperature, while the second was maintained at -80°. The effluent gas was collected in a calibrated receiver.

Table 1 presents the results of experiments carried out at 100° over different portions of catalyst using ethylene-hydrogen mixtures in which the volume ratio of C_2H_4 to H_2 was varied from 1 to 3.2 and the oxygen content was varied from 1 to 1.6%. The data of Table 1 show that at 100°, in addition to hydrogenation of ethylene to ethane, polymerization of ethylene occurred simultaneously with the formation of gaseous dimer and liquid products, the yield of polymerization products reaching 35% of the ethylene fed. Experiments were also carried out

TABLE 1

Catalyst portion	Expt. No.	Expt. duration, hr	In feed gas		Yield, % of ethylene fed		Ethane yield, % of hydrogen fed
			C_2H_4 : H_2	O_2 content, %	liquid hydrocarbons	butylene and butane	
1	1	3,5	3,0	1,0	Trace	20,3	75,2
1	2	5	2,7	1,0	6,2	12,3	58,6
1	3	5	3,2	1,0	11,0	6,8	72,0
1	4	10	3,2	1,4	18,6	8,0	62,7
1	5	15	3,1	1,0	11,5	1,1	48,1
2	6	5	2,7	1,2	7,1	19,0	67,5
3	7	5	2,0	1,6	24,7	12,0	78,0
3	8	5	2,2	1,6	20,9	1,1	37,8
4	9	5	1,1	1,5	16,6	9,7	71,5

TABLE 2

Expt. No.	Expt. duration, hr	React. temp., °C	Yield, % of ethylene fed		Ethane yield, % of hydrogen fed
			liquid hydrocarbons	butylene and butane	
10	6	100	23,7	11,5	45,3
11	15	120	17,4	10,9	56,3
12	10	140	16,3	5,9	66,7
13	10	160	9,4	5,2	72,6
14	15	180	8,2	3,7	78,8
15	10	200	5,4	2,6	82,7
16	10	220	3,0	2,1	79,2

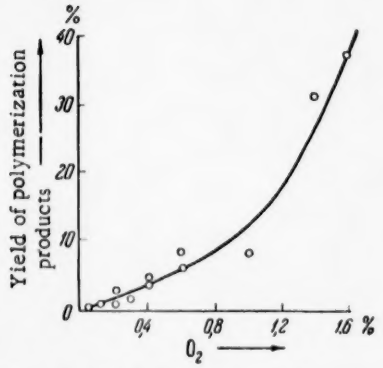
under the same conditions at 100°, but feeding only ethylene containing 0.5 to 1.8% oxygen. It was found that polymerization of ethylene does not occur in the absence of hydrogen. It should be remarked that the effluent gas obtained during polymerization of ethylene at 100° usually contained 1 to 1.5% CO. Therefore, it might be assumed that this reaction is identical with the hydropolymerization of ethylene under the influence of carbon monoxide [2]. In view of the fact that hydropolymerization of ethylene in the presence of carbon monoxide proceeds with maximum yields of reaction products at 190-200° and is accelerated by an increase in the carbon monoxide concentration, it would be expected that polymerization of ethylene in the presence of hydrogen would also be accelerated by an increase in the temperature to 190-200° and by the addition of CO at 100°. The experimental results were in contradiction to this. Table 2 presents the results of experiments carried out at different temperatures over the same portion of catalyst and with the same feed mixture, in which the volume ratio of C_2H_4 to H_2 was 1.1 and the oxygen content was 2%.

It may be seen from the data of Table 2 that with an increase in the reaction temperature from 100° to 220°, the yield of products from the polymerization of ethylene in the presence of hydrogen decreased continuously from 35% at 100° to 5% of the ethylene fed at 200°, with a simultaneous increase in the ethane yield from 45 to 79% of the hydrogen fed. Table 3 presents the results of experiments at different temperatures. These results show the effect of the addition of carbon monoxide on the course of polymerization and hydrogenation. It was found that the addition of 4.4% CO to the $C_2H_4-H_2$ mixture, in which the volume ratio of C_2H_4 to H_2 was 2.4 and the O_2 content was 1.2%, suppressed polymerization and sharply inhibited hydrogenation at 100° (Expt. 17). Appreciable formation of polymerization products began at 120°, and the yield increased with an increase in the temperature. Hydrogenation of ethylene to ethane simultaneously increased. At 190°, the yield of polymerization products amounted to 33% of the ethylene fed, and the ethane yield was 53.5% of the hydrogen fed (Expt. 20). The relationship was reversed in the absence of carbon monoxide: At 100°, the yields of polymerization products and ethane were, respectively, 22 and 67% (Expt. 22); i.e., both reactions proceed rapidly, while at 190° (Expt. 21),

TABLE 3

Expt. No.	Expt. duration, hr	Reaction temp., °C	In feed gas, content, %			Yield of polymerization products, % of ethylene fed	Yield of ethane, % of hydrogen fed
			CO	O_2	$C_2H_4 : H_2$		
17	12	100	4,4	1,2	2,4	0,0	5,9
18	8	120	4,4	1,2	2,4	1,6	9,7
19	12	150	4,4	1,2	2,4	10,4	38,5
20	12	190	4,4	1,2	2,4	32,9	53,5
21	12	190	—	1,2	3,5	5,6	61,2
22*	12	100	—	1,2	3,1	22,2	67,1

* The catalyst was regenerated with hydrogen at 450° for 3 hr before this experiment.



Dependence of the yield of polymerization products at 100° on concentration of oxygen in the feed gas.

hydrogenation proceeded at the same rate, and the yield of ethane was 61%, while polymerization practically ceased (the polymerizate yield of 5.6% must be ascribed to the effect of traces of CO remaining in the reaction system from the previous experiments). Thus, the polymerization of ethylene in the presence of hydrogen at 100° is not the same reaction as the hydropolymerization of ethylene under the influence of carbon monoxide.

The presence of CO in the effluent gas and also the presence of hydrogen peroxide (detected by reaction with titanic acid [4]) in the water produced in the reaction in certain experiments indicates that oxygen present as an impurity in the feed gas actively enters into the reaction through interaction with the major components of the feed. It might be assumed that this results in the formation of active forms on the catalyst surface, which bring about the initial polymerization of the ethylene; in other words, oxygen can behave as a reaction initiator. Obviously, if such an assumption is correct, a change in the concentration of oxygen should have an effect on the course of the reaction, and the exclusion of oxygen from the composition of the feed mixture should lead to the complete absence of polymerization products. This was confirmed by experiment. As may be seen from Fig. 1, in experiments carried out at 100°, the yield of polymerization products increased continuously with an increase in oxygen concentration over the range investigated. In experiments carried out with ethylene–hydrogen mixtures in which the oxygen concentration was less than 0.1%, polymerization was not observed.

All of these data show that the polymerization of ethylene in the presence of hydrogen, a reaction which we were the first to observe and which is accompanied by hydrogenation of the ethylene, takes place at 100° over a cobalt catalyst and is initiated by oxygen.

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ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF SOME AROMATIC AND ALIPHATIC METAL KETYLS IN SOLUTION

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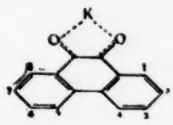
We have previously published investigations of the electron paramagnetic resonance (e.p.r.) spectra of certain metal ketyls [1, 2]. The present paper presents new results obtained in a study of the e.p.r. spectra of solutions of a series of aromatic and aliphatic metal ketyls. Investigation of the e.p.r. spectra of solutions of such compounds is of interest in connection with the possibility of resolving the hyperfine structure (h.f.s.) and thereby forming an estimate of the distribution of the spin density of the unpaired electron in the radical. The aliphatic metal ketyls merit special attention, for these are almost the only representatives of long-lived aliphatic free radicals.

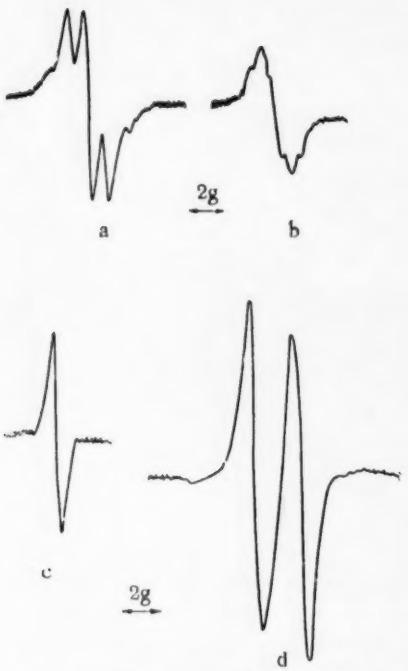
We investigated the e.p.r. spectra of dilute solutions of K phenanthrenequinone ketyl, K benzyl ketyl, K hexamethylacetone ketyl, K diethylpinacolone ketyl, and K triethylpinacolone ketyl in 1, 2-dimethoxyethane.

Unfortunately, K anthraquinone ketyl and K p-quinone ketyl dissolve neither in 1,2-dimethoxyethane nor in tetrahydrofuran.

A five-component h.f.s. (Fig. 1a) with a splitting of 1.1-1.2 gauss was obtained for the K phenanthrenequinone ketyl solution. The spectrum shows that the eight protons of phenanthrenequinone are not all equivalent, but are divided into two different groups of four each. It would appear at first glance that the spectrum does not correspond to that required for four equivalent protons with an intensity ratio of 1 : 4 : 6 : 4 : 1. Pool and Anderson [3] have calculated from theoretical considerations the shape of spectra with h.f.s. for different numbers of equivalent protons and at various ratios of hyperfine interval to line width. For the case in which this ratio is less than or equal to unity, the shape of the spectrum for four equivalent protons is in good agreement with that obtained in the present work. Since h.f.s. of the second order is forbidden to the remaining four protons, the hyperfine components of K phenanthrenequinone ketyl are broad, and this leads to the observed shape of the spectrum. The question arises as to why the experiment gives a quintet for the h.f.s. of K phenanthrenequinone ketyl. The explanation must apparently be sought in the nonequivalent localization of the unpaired electron at all centers from 1 to 8.

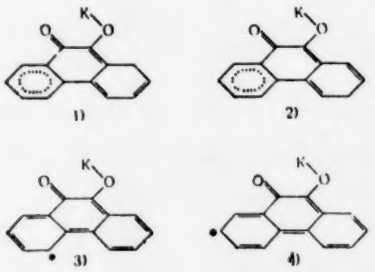
It is possible to visualize the presence of the unpaired electron at four centers in accordance with Schemes 1-4. Calculations show that the resonance energy when the unpaired electron is in position 1 and 3,





E.p.r. spectra: a) K phenanthrenequinone ketyl, b) K benzyl ketyl; c) K hexamethylacetone ketyl, d) K diethylpinacolone ketyl in 1,2-dimethoxyethane.

is greater than the resonance energy of the system in which the electron is present at 5 and 7, the difference amounting to 0.5 β or 8.5 kcal. (with the usual value for the resonance integral).

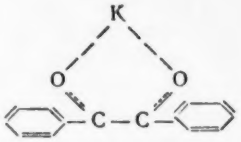


In a similar manner, counting from the other oxygen (since the two oxygens are equivalent in metal ketyls), the presence of the unpaired electron at 6 and 8 corresponds to a resonance energy greater than that with the electron present at 2 and 4, and these two cases again differ by the same amount, 0.5 β. Thus, the four positions 1, 3, 6, and 8 are energetically more favorable, which leads to resolution of the quintet in the spectrum.

Using the empirical equation of McConnell for calculating spin densities ($a = Q\rho$, where a is the splitting factor and Q is -22.5), an approximate calculation (since the spectrum could not be completely resolved) shows that the over-all spin density in the rings is less than in the case of K benzophenone ketyl [2].

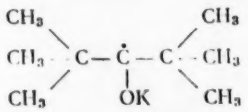
Consequently, these data indicate a significant localization of the unpaired electron at the carbonyl carbons.

Dilute solutions of K benzyl ketyl in 1,2-dimethoxyethane and



in tetrahydrofuran gave spectra in which only seven-component h.f.s. (Fig. 1 b) was noted. It was not possible to obtain good resolution of the spectra, since splitting was very weak (the distance between the component maxima was 0.6-1.7 gauss). However, these spectra indicate that, as in the case of K benzophenone ketyl [2], the ortho and para positions in the benzene rings are equivalent, and the slight separation and narrowness of the absorption lines indicate a still greater localization of the unpaired electron at the carbonyl carbons than in K phenanthrenequinone ketyl.

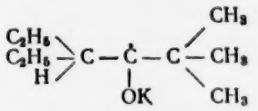
K hexamethylacetone ketyl in dimethoxyethane gave a very sharp singlet signal with a width of 0.5-0.7 gauss; this spectrum was obtained over a fairly broad concentration interval (Fig. 1 c). The narrowness of the line indicates



a greater degree of localization of the unpaired electron at the carbonyl carbon. The absence of h.f.s. is explained

on the basis that in the neighborhood of the carbonyl carbon, on which the unpaired electron is localized, there is no nucleus possessing nonzero spin. There are protons in the molecule, but they are associated with γ-carbons, and it is well known that γ-protons do not cause splitting [4].

Dilute solutions of K diethylpinacolone ketyl gave only a split doublet (2.1 gauss splitting) (Fig. 1d). The splitting is apparently caused by the single β-proton associated with the β-carbon.



K triethylpinacolone ketyl gave a narrow singlet signal with two very low-intensity secondary components. Analysis of the spectrum and a comparison of the spectrum with that of K diethylpinacolone ketyl showed that the low intensity secondary components were due to a very small amount of K diethylpinacolone ketyl. As a matter of fact, the triethylpinacolone ketyl was synthesized by ethylation of diethylpinacolone, and complete removal of the diethylpinacolone during separation of the triethylpinacolone was not possible.

In general, the data for the aromatic metal ketyls show that the distribution of the spin density is in good agreement with the idea of prolonged stabilization of free radicals through delocalization of the unpaired electron in the ring. But it is probable that this delocalization is not the major factor determining the existence of metal ketyls, since the unpaired electron is, to a significant degree, localized at the carbonyl carbon. Data obtained with the aliphatic metal ketyls confirm this assumption.

The authors wish to express their appreciation to I. Yu. Kokoreva, who took part in the experimental work.

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EVIDENCE REFUTING DOUBLE PROTONIZATION OF HYDRAZO COMPOUNDS DURING REARRANGEMENT

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A number of investigations have been published over the past 15 years regarding the kinetics of the rearrangement of hydrazo compounds [1], particularly rearrangement in aqueous alcoholic solutions of HCl. On the basis of these investigations, it has been assumed that the reaction rate in solutions of ionized acids is directly proportional to the first order of the concentration of hydrazo compound and to the square of the hydrogen ion concentration. Consequently, it has been assumed that the transition state complex is formed from a molecule of the hydrazo compound and two protons. This opinion is presently held by almost all authors. However, this interpretation is subject to some objections.

Let us first of all turn to certain material from work on the kinetics of the reaction. Attention is particularly directed to the case of hydrazobenzene. According to the determinations of Carlin, Nelb and Odioso [2], HCl in solution in 95% ethyl alcohol converts hydrazobenzene to a mixture of benzidine and biphenyline in a ratio of 70 : 30; the ratio does not depend on temperature, acid concentration, or over-all concentration of ions. In this case, it is assumed that the hydrazobenzene disappearing is wholly converted to the 70 : 30 mixture of benzidine and biphenyline. Some authors, apparently without justification, have extended this ratio to apply to rearrangements under different conditions, especially in highly dilute aqueous ethyl alcohol. Many of these data are inaccurate.

In the first place, the absolute amount of biphenyline is significantly less than that found by Carlin, Nelb and Odioso; moreover, the ratio of benzidine to biphenyline is closely associated with the concentration of the alcohol: The ratio is 79 : 21 in 95% alcohol, 84 : 16 in 75% alcohol, and 87 : 13 in 45% alcohol (it is 92 : 8 in aqueous HCl). It is true that the ratio of benzidine to biphenyline is almost independent of the concentrations of hydrazo compound and acid; however, with an increase in temperature, the amount of benzidine decreases, owing to the formation of biphenyline and other substances. In the second place, o-aminodiphenylamine (or the analogous o-semidine) is found among the rearrangement products, and the amount of this compound increases with an increase in the alcohol concentration. Finally, rearrangement is always accompanied by intermolecular reactions–disproportionation–the occurrence of which is particularly appreciable in the case of 4,4'-dimethylhydrazobenzene (and analogs with substituents in the 4- and 4,4'- positions). The amount of p-toluidine significantly exceeds the amount of p-azotoluene, which is due to the fact that the alcohol is also somewhat of a reducing agent for the monoprotonated hydrazo compound.

• We previously found that if 2,2'-dimethoxyhydrazobenzene is added to an equimolar amount of hydrazobenzene hydrochloride (0.01 mole) in ether at 0° and the mixture is allowed to stand for a day, neither aniline nor benzidine is found in the product. In addition to partially regenerated hydrazobenzene and products of the rearrangement of the 2,2'-dimethoxyhydrazobenzene, we found 2,2'-dimethoxyazobenzene (0.130 g), azobenzene (0.526 g), and o-anisidine (0.787 g).

Expt. No.	Hydrazo compounds	Alcohol concentration, %	Obtained, %					Total of all substances, %
			benzidines	biphenylines	o-semidines	anilines	azo compounds	
1	I	99,9	75,5	19,0	2,3	1,3	1,3	99,4
2	I	95,0	72,7	19,6	2,0	2,1	2,2	98,6
3	I	95,0	73,0	19,4	2,2	2,3	2,4	99,3
4	I	95,0	56,5	23,8	2,6	8,1	8,0	99,0
5	I	85,0	79,0	16,9	1,4	1,1	1,1	99,5
6	I	75,0	81,2	15,2	1,0	1,1	1,1	99,6
7	I	75,0	80,5	15,4	1,2	1,1	1,1	99,3
8	I	60,0	83,2	13,5	0,9	0,9	0,9	99,4
9	I	45,0	84,3	12,6	0,7	0,9	1,0	99,5
10	I	—	89,8	7,7	0,2	0,9	0,9	99,5
11	II	95,0	87,0	10,9	0,7	0,5	0,5	99,6
12	III	95,0	—	—	58,1	23,0	16,1	97,2
13	IV	99,9	65,7	16,9	2,6	4,7	4,5	94,4

In the cases considered above, disproportionation and rearrangement of the hydrazo compounds are closely associated reactions; however, it is completely incorrect to assume, as did Carlin and Wich [4], that the action of a proton is required for disproportionation of a monoprotonated hydrazo compound.

The results obtained in a study of the rearrangement of hydrazobenzene (I) and analogs are presented in Table 1. In one series of experiments, the solution of hydrazobenzene (0.01 mole) in alcohol was rapidly cooled under nitrogen and was then mixed all at once with the solution of HCl (0.1 mole); the total volume was 100 ml. The mixture was held for 2 hr at 0°, and the crystals of benzidine were then separated and converted to the sulfate. The alcohol was evaporated at 10-20°, the residue was diluted with water, most of the acid was carefully neutralized, and the o-semidine and azobenzene were extracted with ether [5]. The rest of the benzidine, the biphenyline, and the aniline were contained in the aqueous fraction. The benzidine sulfate was reprecipitated. The total biphenyline and aniline was established by diazotization, and the amount of aniline was determined after a second steam distillation.

In Expt. 4, the (I) was added to the acid solution at 45-50° over a period of 15 min. The reagent concentrations were reduced in Expts. 2 and 7; the hydrazobenzene (0.01 mole) was added uniformly over a period of 4 hr to a solution of HCl (0.04 mole) in alcohol (200 ml) at 0°, and the mixture was allowed to stand for 16 hr. In Expt. 10, the (I), in solution in a mixture of benzene and toluene, was extracted with an aqueous solution of HCl (0.1 mole in 60 ml) at 0°.

2,2'-Dimethylhydrazobenzene (II), 4,4'-dimethylhydrazobenzene (III), and 2,2'-dimethoxyhydrazobenzene (IV) were added uniformly over a period of half an hour to a solution of HCl (0.1 mole) in alcohol (100 ml) at 0°. The treatment of the mixture was similar to that described for (I) (see also [5]).

The results of the rearrangement of (IV) differed considerably from the results of Ingold and Kidd [6], who did not find the isomeric o-dianisidine. We may add that the anisidine base, which was obtained by the action of ammonia on the hydrochloride, melted at 133-135° (and not at 138°!) and contained about 4% impurities, predominately the isomeric biphenyline, which was separated by special treatment [5].

Let us pause to consider the interpretation of the results presented in the article by Bunton, Ingold, and Mhala [7]. The authors reported that the kinetic order of the reaction with respect to hydrogen ions was 1.85 in the case of hydrazobenzene and 1.6 and 2.0, respectively, for 2,2'-dimethyl- and 3,3'-dimethylhydrazobenzene. Carlin and Odioso [8] explained the deviations from the expected value of two on the basis that during the reaction a considerable part of the hydrazo compound occurs combined with a molecule of acid. Along this same line, Bunton, Ingold, and Mhala posed the question of whether the Hammett function* should not be used instead of the acid concentration in determining the kinetic order of the reaction. Blackadder and Hinshelwood [9], basing their thoughts on the case of 2,2'-dimethylhydrazobenzene, considered that certain monoprotonated hydrazo compounds undergo some rearrangement spontaneously.

* The acidity function, which characterizes the tendency of the medium to transfer a proton to a neutral base.

On the basis of recent investigations, it seems to us that these questions require a different answer. It has been shown [10] that when hydrazobenzene and its closest analogs are heated (110°) with amine hydrochlorides (sometimes with small amounts of weak acids), they disproportionate rapidly, and the amounts of rearrangement products are insignificant, as a rule. Evidently, traces of HCl combine with the hydrazo compound, after which the following reaction takes place:

$$2\,(RNH-\overset{+}{N}H_2R)\,\bar{Cl} \rightarrow RN=NR + 2R\overset{+}{N}H_3\bar{Cl}. \qquad (1)$$

Thus, regardless of the structure of the hydrazo compound, the monoprotonated molecule has the ability very readily to undergo reduction and oxidation, and a tendency toward spontaneous rearrangement, as proposed by Blackadder and Hinshelwood, is not observable. However, as will be seen, such an assumption is completely unnecessary.

Further, familiarity with the stability of salts of hydrazo compounds under the conditions of their preparation [5] suggests certain conclusions. It has been established that hydrazobenzene and its analogs with substituents in the 2-, 3-, and 3,3'-positions form relatively stable salts (they rearrange comparatively slowly under the conditions of their preparation), and as a consequence they can be isolated, occasionally in very good yield. On the contrary, hydrazo compounds with substituents in the 2,2'- and 4,4'-positions do not form stable salts. Moreover, there are frequent cases in which salts of more basic hydrazo compounds (particularly hydrazobenzene hydrochloride) rearrange more difficultly than do salts of less basic hydrazo compounds.

Considering the material presented above, it is clear that if those hydrazo compounds which form relatively stable salts can be to some extent likened to diacidic bases of the usual type with respect to their behavior toward acids, in the remaining cases the difference in the rates of monoprotonization and subsequent rearrangement can be so small that the kinetic order of the rearrangement with respect to hydrogen ions approaches the expected figure of two only accidently, if at all.

Turning now to the question of just how probable it is that double protonization is required for rearrangement, we note, first of all, that it was shown [11] a comparatively long time ago that "hydrazobenzene dihydroiodide" [12] is not a real compound (and similarly for "hydrazobenzene dihydrochloride" [3]), a fact which certain authors have supported [13]. We have recently become persuaded that in the significantly more basic hydrazine series—the aliphatic-aromatic hydrazines—it is not possible to prepare appreciable amounts of diacidic salts, even under very vigorous conditions, for example, by the action of hydrogen bromide (0.004 mole) at 0° on a solution of N-methyl-N'- phenylhydrazine (0.001 mole) in a mixture of benzene and toluene (20 ml). Under precisely the same conditions, 2,2'-dichlorohydrazobenzene—a significantly weaker base than pentachloroaniline— very rapidly undergoes rearrangement (see also reference [5]). It is evident that such a high rate of rearrangement cannot be due to insignificant traces of the doubly protonated hydrazo compound, yet only such amounts of the latter compound could be present in this case.

We note the following additional facts. There exist hydrazo compounds, for example 2,2-dimethoxyhydrazobenzene, which react rapidly and vigorously when introduced in uniformly small portions into 85% or glacial acetic acid at 20°. On the other hand, 3,3'-dichlorohydrazobenzene, for example, is incapable of rearranging even when heated (110°) with these acids; only about 2.5% of the hydrazo compound disproportionates when it is heated for half an hour. Thus, even single protonization [10] of 3,3'-dichlorohydrazobenzene in acetic acid proceeds with difficultly. If it is recalled that the difference in the basicities of the original and monoprotonated hydrazo compound is very great, while 3,3'-dichloro- and 2,2'-dimethoxyhydrazobenzenes are not so greatly differentiated with respect to basicity (the difference in the corresponding pK values apparently does not exceed 2-2.5 units [5]), it becomes clear that the requirement of double protonization of 2,2'-dimethoxyhydrazobenzene under the above conditions is without basis.

In view of all this, during our study of rearrangements in un-ionized acid media we arrived at a mechanism based on an intermolecular interaction between the monoprotonated hydrazo compound and the acid, resulting in the following transition state:

$$(RNH-\overset{+}{N}H_2R)\,\bar{X}\ldots HX. \qquad (2)$$

In cases where the acid is ionized, the interesting proposal of Blackadder and Hinshelwood merits attention; these authors considered that monoprotonated hydrazo compounds rearrange upon just the approach of a proton.

For aqueous and aqueous alcoholic solutions, we have:

$$RNH - \overset{+}{N}H_2R\ H_3\overset{+}{O}. \qquad (3)$$

The ethoxonium ion is the catalyst for the reaction in absolute or nearly absolute alcohol; it is important that although the rate of the reaction in 99.9% alcohol was approximately 150 times higher than in 95% alcohol, the results of the rearrangement of hydrazobenzene were almost the same (compare Expts.1 and 3).

L. G. Krolik took part in the experimental work.

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ORGANOBORON COMPOUNDS

THE REACTION OF 1,2-DIARYLDIBORANES WITH OLEFINS AND DIOLEFINS

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The method previously proposed by the present authors for the preparation of 1,2-diaryldiboranes from esters of arylboronic or diarylborinic acids and diborane [1] makes these interesting compounds available for study.

The chemical properties of these compounds are almost uninvestigated. It is known that 1,2-diphenyldiborane forms complex compounds with pyridine and trimethylamine, and the action of methyl alcohol converts it to the dimethyl ester of phenylboronic acid [2].

We have investigated the reactions of 1,2-diaryldiboranes with olefins and diolefins. 1,2-Diphenyldiborane reacts with olefinic hydrocarbons—propylene or 1-butene—in cold ether solution. The resulting phenyldialkylborines are unstable, and even at room temperature they rapidly undergo symmetrization to triphenylborine and trialkylborines.

$$3\,(C_6H_5BH_2)_2 + 12\,CH_2{=}CH-R \rightarrow 6C_6H_5B\begin{matrix}\diagup\,CH_2-CH_2-R\\ \diagdown\,CH_2-CH_2-R\end{matrix} \rightarrow$$

$$\rightarrow 2\,(C_6H_5)_3B + 2B(CH_2-CH_2-R)_3$$

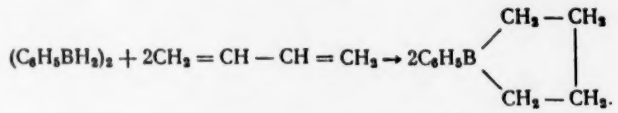
$$R = CH_3,\ C_2H_5$$

Thus, in the experiment with propylene, removal of the solvent by vacuum distillation left a mixture of a liquid and crystalline triphenylborine. Distillation of this mixture on the following day gave only tri-n-propylborine and triphenylborine. The products of the reaction between diphenyldiborane and 1-butene were separated immediately upon completion of the experiment. After separation of the triphenylborine, distillation of the remaining liquid yielded fractions with wide boiling ranges which were higher than the boiling point of tri-n-butylborine; this indicated the presence of phenyl-di-n-butylborine. However, further fractionation was accompanied by symmetrization, and, as a result, only triphenylborine and tri-n-butylborine were obtained. The possibility cannot be excluded that part of the triphenylborine was formed by symmetrization of the original 1,2-diphenyldiborane during the course of its reaction with the olefinic hydrocarbons.

The reaction of 1,2-diaryldiboranes with diolefinic hydrocarbons was carried out in benzene or toluene solution at -40 to -30°. The 1,2-diaryldiboranes used in the present work were 1,2-diphenyldiborane and 1,2-di-o-tolyldiborane; this represents the first time the latter compound has been synthesized. The ditolyldiborane was prepared in 51% yield by passing diborane into an ether solution of isobutyl di-o-tolylborinate:

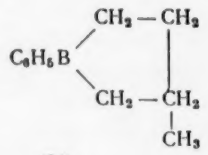
$$3\,(o\text{-}CH_3C_6H_4)_2BOC_4H_9\text{-iso} + 2B_2H_6 \rightarrow 3\,(o\text{-}CH_3C_6H_4BH_2)_2 + (\text{iso-}C_4H_9O)_3B.$$

The action of 1,2-diphenyldiborane on butadiene gave a 51% yield of a cyclic compound with a boron atom atom in the ring—1-phenylborocyclopentane [1-phenylborolane] (I):

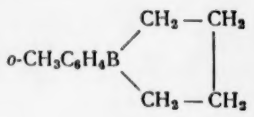


(I)

The addition of 1,2-diaryldiboranes to other dienes also takes place in a similar manner. Thus, the action of 1,2-diphenyldiborane on isoprene gave 1-phenyl-3-methylborocyclopentane (II), and 1-o-tolylborocyclopentane (III) was synthesized from 1,2-di-o-tolyldiborane and butadiene:



(II)



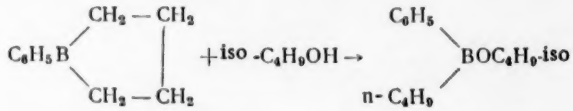
(III)

Moreover, these conversions are accompanied by the formation of triarylborines, which indicates partial symmetrization of the original 1,2-diaryldiboranes during the course of the reaction.

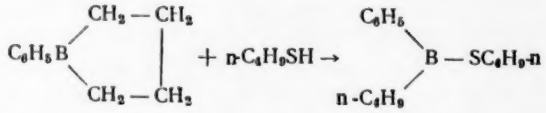
1,2-Diphenyldiborane reacts at -40° with cyclopentadiene. This yields a solid, high molecular weight substance which is insoluble in ether and very slightly soluble in benzene.

1-Phenylborocyclopentane has previously been prepared by the action of phenylboron difluoride on 1,4-tetramethylenedilithium [3]. The formation of a cyclic compound, 1,1-diborocyclopentanebutane [1,1'-tetramethylenebisborolane] during the action of diborane on butadiene was observed by Köster [4].

It appeared to be of interest to investigate the behavior of 1-arylborocyclopentanes with compounds with an active hydrogen. It was found that 1-phenylborocyclopentane reacts more readily with isobutyl alcohol than do trialkylborines [5]. The reaction proceeds with rupture of the ring to form the isobutyl ester of n-butylphenylborinic acid:



1-Phenylborocyclopentane is converted by the action of n-butyl mercaptan to the n-butyl ester of n-butylphenylthioborinic acid, which is the first representative of esters of alkylarylthioborinic acids.



EXPERIMENTAL

All operations were carried out in an atmosphere of dry nitrogen.

1,2-Di-o-tolyldiborane. Diborane, obtained from 10.2 g of $NaBH_4$ and 35 ml of boron trifluoride etherate in ether, was passed into a solution of 20.6 g (0.077 mole) of isobutyl di-o-tolylborinate in 25 ml of ether. The ether was distilled, and the residue was carefully washed with cold ether and hexane. There was obtained 8.2 g (51%) of 1,2-di-o-tolyldiborane in the form of colorless crystals with an m.p. of 53-55°.

Found %: B 10.10; $CH_3C_6H_4$ 87.40.
C_7H_9B. Calculated %: B 10.40; $CH_3C_6H_4$ 89.60.

1,2-Di-o-tolyldiborane dissolves readily in ether, hexane, and benzene. It reacts violently with alcohol with the evolution of hydrogen.

Reaction of 1,2-diphenyldiborane with propylene. Propylene was passed into a solution of 5.4 g (0.03 mole) of 1,2-diphenyldiborane in 80 ml of absolute ether, which was cooled to -20 to -10°. The solvent was distilled under vacuum. On the following day, the crystalline precipitate was filtered and washed with isopentane. There was obtained 2.8 g of triphenylborine with an m.p. of 137-145°. Distillation of the filtrate gave 4.3 g of tripropylborine with a b.p. of 26-32° at 2 mm; $n^{20}D$ 1.4158. The crystalline precipitate, 1.7 g, was triphenylborine, which, after being washed with hexane, had an m.p. of 133-140°.

Reaction of 1,2-diphenyldiborane with 1-butene. 1-Butene was passed into a solution of 4.4 g (0.024 mole) of 1,2-diphenyldiborane in 70 ml of absolute ether cooled to -5 to 0°. The solvent was distilled under vacuum, and the crystalline precipitate was filtered and washed with isopentane. There was obtained 0.7 g of triphenylborine with an m.p. of 137-145°. The following fractions were obtained upon distillation of the filtrate: 1) 55-75° at 2.5 mm, 2.4 g; 2) 75-100° at 2.5 mm, 3.7 g; 3) 2.5 g of a crystalline residue. When distilled a second time, almost all of the first fraction came over at 59-62° at 2 mm. The boiling point of the second fraction during a second distillation was 59-70° at 2 mm; the residue contained 0.5 g of a crystalline material. During the subsequent distillation, almost all of this fraction boiled at 59-61° at 2 mm; $n^{20}D$ 1.4268. Thus, all of the liquid reaction products were tributylborine. The crystalline residue was identified as triphenylborine; after it had been washed with hexane, it had an m.p. of 134-139°.

1-Phenylborocyclopentane (I). A four-neck flask fitted with a stirrer, two dropping funnels, and a condenser was covered with a mixture of solid carbon dioxide and acetone having a temperature of -30°. The condenser was also cooled with the mixture of solid carbon dioxide and acetone. A solution of 8.4 g (0.047 mole) of 1,2-diphenyldiborane in 90 ml of toluene and 6.5 g (0.12 mole) of butadiene were added, with stirring, to the flask. Upon completion of the addition, the reaction mixture was allowed to come to room temperature and to stand at this temperature for 1 hr. The solvent was distilled under vacuum. The resulting precipitate was filtered and washed with isopentane. There was obtained 1.3 g of triphenylborine with an m.p. of 125-138°.

Found %: B 4.33. $C_{18}H_{15}B$. Calculated %: B 4.47.

The ammoniate of the triphenylborine had an m.p. of 226-228°.

The filtrate remaining after separation of the triphenylborine was fractionated. There was obtained 6.8 g (51%) of 1-phenylborocyclopentane with a b.p. of 58-62° at 2 mm. After an additional distillation, the substance had a b.p. of 50-51° at 1 mm; d^{20}_4 0.9239; $n^{20}D$ 1.5278; MR_D found 48.00; calculated, 48.17.•

1-o-Tolylborocyclopentane (III). The synthesis was carried out in a manner similar to that used for preparation of 1-phenylborocyclopentane. The reaction was carried out with 8.7 g (0.042 mole) of di-o-tolyldiborane in 80 ml of toluene and 9 ml of butadiene. The solvent was distilled and the residue was fractionated. There was obtained 6.8 g (51%) of 1-o-tolylborocyclopentane with a b.p. of 65-70° at 1.5 mm. In a second distillation, the material had a b.p. of 63-65° at 1 mm; d^{20}_4 0.9370; $n^{20}D$ 1.5429; MR_D found 53.08; calculated, 52.83.

Found %: C 83.47; H 9.75; B 6.98
$C_{11}H_{15}B$. Calculated %: C 83.58; H 9.57; B 6.85.

1-Phenyl-3-methylborocyclopentane (II). A solution of 10.9 g (0.06 mole) of 1,2-diphenyldiborane in 60 ml of benzene and a solution of 8.5 g (0.125 mole) of isoprene in 12 ml of benzene were gradually mixed; the mixture was cooled with ice water as the two reactants were mixed. The solvent was distilled and the residue was fractionated. There was obtained 7.6 g (40%) of 1-phenyl-3-methylborocyclopentane with a b.p. of 61-64° at 2 mm; d^{20}_4 0.9083; $n^{20}D$ 1.5205; MR_D found 52.95; calculated, 52.83.

Found %: C 83.10; H 9.56; B 6.82
$C_{11}H_{15}B$. Calculated %: C 83.58; H 9.57; B 6.85

• The refractivities of the aliphatic B-C and aromatic B-C bonds were taken as 1.75 and 2.96, respectively [6].

The action of isobutyl alcohol on 1-phenylborocyclopentane. The isobutyl ester of n-butylphenylborinic acid. To 5.0 g (0.035 mole) of 1-phenylborocyclopentane was added dropwise 3.5 ml (0.040 mole) of isobutyl alcohol. The mixture was then refluxed for 30 min. The isobutyl ester of n-butylphenylborinic acid was separated from the complex mixture of reaction products by distillation; the yield was 2.4 g (30%) of a substance with a b.p. of 92-93° at 2 mm, d^{20}_4 0.8870; $n^{20}D$ 1.4809 was previously reported by B. M. Mikhailov and P. M. Aronovich [7].

The action of n-butyl mercaptan on 1-phenylborocyclopentane. The n-butyl ester of n-butylphenylthioborinic acid. To 6.6 g (0.046 mole) of 1-phenylborocyclopentane was added dropwise 5.5 ml (0.052 mole) of n-butyl mercaptan, and the mixture was heated for 15 min at 70-80°. Fractional distillation of the mixture of reaction products gave a fraction with a b.p. of 107-111° at 1.5 mm; the yield was 4.4 g (39%). In a second distillation, this fraction, which was the n-butyl ester of n-butylphenylborinic acid, had a b.p. of 107-108° at 1.5 mm; $n^{20}D$ 1.5252; d^{20}_4 0.9296.

Found %: C 77.53; H 10.12
$C_{14}H_{23}SB$. Calculated %: C 77.81; H 9.90

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•Original Russian pagination. See C. B. translation.

THE USE OF CHEMICAL CHANGES OCCURRING DURING BETA DECOMPOSITION OF RaE FOR THE SYNTHESIS OF POLONIUM HETEROORGANIC COMPOUNDS

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The ability to form organic derivatives with specific properties is a very important characteristic of an element. The exceptional progress which has been made during recent years in the chemistry of heteroorganic compounds in general has almost ignored a number of elements such as francium, astatine, and polonium. Nevertheless, these elements possess the ability to form heteroorganic compounds--an ability which undoubtedly results from their position in the periodic system and also from the general regularities first noted by D. I. Mendeleev and formulated in their present state by A. N. Nesmeyanov [1, 2].

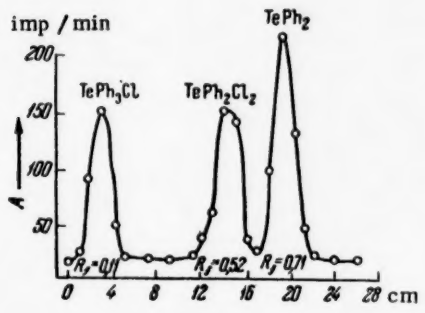

Fig. 1.

The aim of the present work was to develop new methods for the synthesis of certain previously unknown heteroorganic compounds of polonium. Up to the present time, only three papers devoted to the experimental study of this question have appeared in the literature [3-6]. One effective method of synthesis is that based on the use of the chemical changes occurring during beta decomposition processes. We have previously used similar methods for the synthesis of various organometallic compounds of bismuth [7-11].

It was shown in the present work that heteroorganic compounds of polonium (RaF) are formed during beta decomposition of RaE which has been introduced into certain aromatic derivatives.

The polonium compounds were formed as a result of beta decomposition occurring in crystals of $Bi(RaE)Ph_3$ and $Bi(RaE)Ph_3Cl_2$. In order to obtain these compounds with sufficiently high specific activity, use was made of the chemical changes occurring during beta decomposition of RaD in $RaDPh_4$.

The problem lay in the separation and identification of the daughter compounds of polonium (RaF). The basic method used was ascending paper chromatography. A reference substance was necessary to establish the positions of the various polonium heteroorganic compounds on the chromatogram, and the analogous compounds of tellurium—$TePh_2$, $TePh_2Cl_2$, and $TePh_3Cl$—labeled with Te^{127} [12-15] were used for this purpose. Separation of the polonium heteroorganic compounds was carried out in the presence of microgram amounts of these indicators. Analysis of the chromatograms was carried out radiometrically using the alpha activity of polonium and the beta

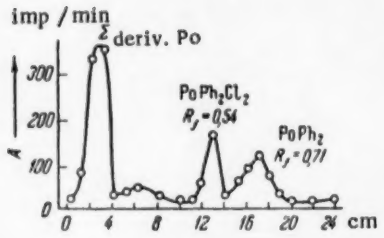

Fig. 2.

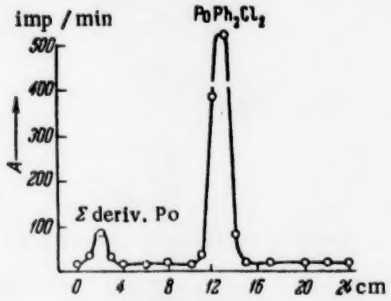

Fig. 3.

activity of Te^{127}. The results of the measurements are plotted in Fig. 1, in which activity is plotted along the ordinate and the distance from the place at which the mixture to be analyzed was applied is plotted along the abscissa. The polonium compound to which an alpha active peak on the chromatogram belonged was established by a comparison of the position of the peak with the position of the peak of the analogous beta-active tellurium derivative. Use of this method is justified by the closeness of the chemical properties of polonium and tellurium. Moreover, when these elements are component parts of complex heteroorganic compounds, the individual properties are still more similar.

The following solvents were found to be the most suitable for the separation of tellurium heteroorganic compounds and consequently, polonium compounds: ethyl acetate (preliminary treatment of the paper with a 25% alcoholic solution of formamide), carbon tetrachloride, and petroleum ether.

The following R_f values were obtained when the tellurium heteroorganic compounds were chromatographed in ethyl acetate (Fig. 1): $TePh_3Cl$, ~ 0.1; $TePh_2Cl_2$, 0.50-0.55; $TePh_2$, 0.70-0.75. When these compounds were chromatographed in carbon tetrachloride (without pretreatment of the paper), the following R_f values were obtained: $TePh_3Cl$, ~ 0; $TePh_2Cl_2$, 0.6-0.7; $TePh_2$, ~ 1.

In petroleum ether, movement with the solvent front occurred only for $TePh_2$. The use of the several solvents considerably increased the reliability of the results, which is particularly important for identification of new compounds.

The distribution of alpha activity between the different chemical forms of polonium as the polonium accumulated in crystals of $Bi(RaE)Ph_3$ is shown in Fig. 2 for the case in which ethyl acetate was used as the chromatographic solvent. The over-all picture of the polonium distribution is characterized by the following data: $PoPh_2Cl_2$, 15 ± 6%; $PoPh_2$, 24 ± 6%; and total remaining polonium derivatives, 61 ± 6%. Chromatographing in carbon tetrachloride gave the following polonium distribution: $PoPh_2Cl_2$, 19 ± 6%; $PoPh_2$, 18 ± 6%, and total remaining polonium derivatives, 63 ± 6 %. When petroleum ether was used as the solvent, the amount of polonium as $PoPh_2$ was 19 ± 6%.

When the polonium was formed in crystals of $Bi(RaE)Ph_3Cl_2$, no $PoPh_2$ was found. In this case, almost all of the polonium (92 ± 3%) occurred in the form of $PoPh_2Cl_2$.

The results obtained when ethyl acetate was used as the solvent are shown in Fig. 3 (R_f = 0.54).

As may be seen from the results of the present work, the chemical state of the RaE exerts a strong effect on the yields of the various forms of RaF. This makes possible the use of the chemical changes occurring during beta decomposition for the synthesis of specific heteroorganic compounds.

In conclusion, the authors wish to take this opportunity to thank Corresponding Member AN SSSR G. A. Razuvaev for valuable advice and observations and B. K. Preobrazhenskii for much advice and aid in questions relating to chromatographic methods of separation.

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HYDROXYFERROCENES AND THEIR DERIVATIVES

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We have already reported the synthesis of hydroxyferrocene through the action of copper acetate on ferrocenylboric acid and haloferrocenes [1]. The ferrocenyl acetate formed in this reaction was hydrolyzed with a base to obtain hydroxyferrocene; a number of its ethers were prepared.

TABLE 1

Neutralization, %	pH	pK	K
30	9,71	10,09	$8,12 \cdot 10^{-11}$
50	10,12	10,15	$7,15 \cdot 10^{-11}$
70	10,57	10,28	$5,30 \cdot 10^{-11}$

Ferrocenyl allyl ether is easily prepared by heating hydroxyferrocene with allyl bromide in acetone in the presence of potassium carbonate. All of our attempts to carry out Claisen rearrangement were unsuccessful and showed that this compound cannot undergo rearrangement. This is probably connected with the incapability of ferrocene to exist in a "quinoid" structure in the transition state. When ferrocenyl allyl ether is heated at 215-220° (under nitrogen) it decomposes to hydroxyferrocene. Part of the ether is recovered unchanged from this reaction. Claisen and Tietze [2] showed some time ago that when allyl ethers of certain phenols (2,4-dimethyl-6-allylphenol and 2,4-dimethyl-6-propylphenol, in which allyl rearrangement is impossible) are heated, they yield the corresponding phenol, and allene and biallyl are liberated.• Allyl rearrangement of the allyl ether of α-naphthohydroquinone under conditions such that the product is simultaneously acetylated has been reported [3], but ferrocenyl allyl ether does not rearrange even under these conditions.

Allylferrocenyl acetate is not formed when ferrocenyl allyl ether is heated in diethylaniline in the presence of acetic anhydride, and the ferrocenyl allyl ether is recovered unchanged.

The above considerations relating to the instability of the "quinoid" state in the ferrocene molecule are supported by experiments on air oxidation of 1,1'-dihydroxyferrocene; the molecule decomposed with the liberation of an inorganic iron compound, and the resulting cyclopentadienone was isolated as the dimer.

In the present paper, the dissociation constants of hydroxyferrocene and phenol are compared, and 1,1'-dihydroxyferrocene and its derivatives are described. The dissociation constants were calculated by the formula of Kumler [4]. The pH measurements were carried out using a glass electrode and an LP-5 potentiometer; they were made at 17° in 0.005 molar solutions of hydroxyferrocene or phenol in 5% alcohol, partially neutralized (30, 50, and 70%) with sodium hydroxide. The data obtained with hydroxyferrocene are presented in Table 1.

•Note added in proof. In an article which has just appeared [7], Fahrni, Habich and Schmid reported that the allyl group in 2,4,6-trimethylphenyl allyl ether shifts to the meta position under the influence of $BiCl_3$. The authors proposed that in this case the first stage of the reaction is the formation of a quinoid form.

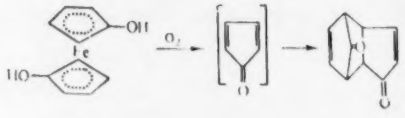
Average values were: for hydroxyferrocene $K = 6.9 \cdot 10^{-11}$, pK 10.17 ± 0.10; for phenol, $K = 1.20 \cdot 10^{-10}$, pK 9.93 ± 0.05. Thus, hydroxyferrocene is a weaker acid than phenol. The difference in the pK values for hydroxyferrocene (with an increase in neutralization) is possibly due to instability of the compound.

We were able to synthesize derivatives of 1,1'-dihydroxyferrocene by using 1,1'-ferrocenylenediboric acid. 1,1'-Ferrocenylenediboric acid reacts with copper acetate with the formation of 1,1'-ferrocenylene diacetate (m.p. 55-56°) in a yield of 41%. This ester of 1,1'-dihydroxyferrocene was obtained in considerably greater yield (83%) if one $B(OH)_2$ group in the 1,1'-ferrocenylenediboric acid was first replaced by a halogen. A method for the preparation of 1-(1'-haloferrocenyl)boric acid was described in our previous article [5]. The action of copper acetate on the latter resulted in substitution of an acetoxy group for both the halogen and the $B(OH)_2$ group. 1,1'-Dibromoferrocene can also be used for the synthesis of 1,1'-ferrocenylene diacetate:

$$\left.\begin{array}{l}(HO)_2BC_5H_4FeC_5H_4B(OH)_2\\ XC_5H_4FeC_5H_4B(OH)_2\\ XC_5H_4FeC_5H_4X\end{array}\right\} \xrightarrow{Cu(OCOCH_3)_2} (CH_3COOC_5H_4)_2Fe,$$

where X is halogen.

The infrared spectrum of ferrocenylene diacetate showed no frequencies characteristic of an unsubstituted cyclopentadienyl ring in ferrocene. Hydrolysis of this compound (in a nitrogen atmosphere) and subsequent acidification or treatment with CO_2 gave yellow needles of 1,1'-dihydroxyferrocene, which is extremely sensitive to air.



It proved to be impossible to use the alkaline hydroxylate for the preparation of derivatives of 1,1'-dihydroxyferrocene [1,1'-dimethoxyferrocene, 1,1'-ferrocenylene dibenzoate, 1,1'-ferrocenylene dibenzenesulfonate, O,O'-(1,1'-ferrocenylene)diglycolic acid].

All of these 1,1'-dihydroxyferrocene derivatives are stable in air.

TABLE 2

	Yield, %	M. p., °C
$(CH_3OC_5H_4)_2Fe$	95	35—36
$(CH_3COOC_5H_4)_2Fe$	83	55—56
$(C_6H_5COOC_5H_4)_2Fe$	68	114—115
$(C_6H_5SO_2OC_5H_4)_2Fe$	72	119,5—120,5
$(HOOC—CH_2OC_5H_4)_2Fe$	76	168,5—169,5

EXPERIMENTAL

Ferrocenyl allyl ether. A mixture of 0.30 g of hydroxyferrocene, 1.5 g of powdered potassium carbonate, and 0.5 ml of allyl bromide in 7 ml of acetone was stirred and heated (under nitrogen) on a water bath for 2 hr. The mixture was then diluted with water and extracted with ether; the ether was filtered, carefully washed with 10% KOH and with water, and evaporated. The resulting yellow oil crystallized on cooling. There was obtained 0.30 g (84% of theoretical) of ferrocenyl allyl ether with an m.p. of 26.5-28°; after recrystallization from a saturated (at room temperature) solution in methyl alcohol by cooling with a dry ice–acetone mixture, the ferrocenyl allyl ether had an m.p. of 28-30°.

Found %: C 64.49; 64.62; H 5.90; 5.98; Fe 22.70; 22.78
$C_{13}H_{14}FeO$. Calculated %: C 64.50; H 5.83 Fe 23.07

Ferrocenyl allyl ether (0.55 g) was heated (under nitrogen) at 215-220° for half an hour. It was cooled to a dark melt, and ether and 10% KOH were then added. The mixture was filtered from the tar. The aqueous layer was separated and extracted with benzoyl chloride. There was obtained 0.17 g of ferrocenyl benzoate with an m.p. of 105-106°; after recrystallization from alcohol, the material melted at 108.5-109.5°. A mixture with a known sample melted without depression of the melting point. The yellow oil remaining after evaporation of the ether was chromatographed over Al_2O_3 in a mixture of ether and benzene. Some time after the solvent had been removed, the oil crystallized. There was obtained 0.22 g of a material with an m.p. of 21-23°. After

recrystallization from hexane the material melted at 27-28°; a mixture with a known sample of ferrocenyl allyl ether melted at this same temperature.

Ferrocenehydroxyacetic acid. A solution of 0.42 g of chloroacetic acid was added to 0.42 g of hydroxyferrocene in 3 ml of KOH solution, and the mixture was refluxed for 3 hr. (The mixture was kept alkaline during the reaction.) The mixture was cooled, and crystals of the potassium salt crystallized; the solution was made acid with 10% H_2SO_4 and extracted with ether until the precipitated potassium salt disappeared. The ether was washed with water and evaporated. The remaining crystals were carefully dried under vacuum over P_2O_5. There was obtained 0.44 g (82% of theoretical) of ferrocenehydroxyacetic acid with an m.p. of 131-133°; recrystallization from benzene gave a material which melted at 136-137°.

Found %: C 55.59; 55.39; H 4.77; 4.78; Fe 21.50; 21.56
$C_{12}H_{12}FeO_3$. Calculated %: C 55.41; H 4.65; Fe 21.48

1,1'-Ferrocenylene diacetate. a) To a hot solution of 2 g of 1-(1'-bromoferrocenyl)boric acid was added a solution of 5.4 g of copper acetate. The mixture was heated to boiling. A red precipitate of cuprous oxide formed. The mixture was cooled and extracted with ether, and the ether extract was washed with 5% KOH and with water and then dried, There was obtained 1.62 g (83% of theoretical) of 1,1'-ferrocenylene diacetate with an m.p. of 50-52°. After recrystallization from hexane, the material melted at 55-56°.

In a similar manner, 0.66 g (70% of theoretical) of 1,1'-ferrocenylene diacetate was obtained from 0.83 g of 1-(1'-chloroferrocenyl)boric acid and 2.2 g of copper acetate.

b)* To a hot suspension of 2 g of 1,1'-ferrocenylenediboric acid in 400 ml of water was added a solution of 5.8 g of copper acetate. The mixture was heated for 40 min on a boiling water bath. A red precipitate formed. The 1,1'-ferrocenylene diacetate was extracted with ether, and the ether extract was washed with water and evaporated. The residue (0.92 g) was dried and washed on a filter with petroleum ether. Evaporation of the petroleum ether gave 0.90 g (41% of theoretical) of 1,1'-ferrocenylene diacetate with an m.p. of 48-51°; after recrystallization from hexane, the material melted at 54.5-55.5°. A mixture of this material with a sample of that obtained in Expt. (a) melted without depression of the melting point.

Found %: C 55.63; 55.55; H 4.72; 4.70; Fe 18.63; 18.58
$C_{14}H_{14}FeO_4$. Calculated %: C 55.66; H 4.67; Fe 18.49

Hydrolysis of 1,1'-ferrocenylene diacetate (in a nitrogen atmosphere). 1,1'-Ferrocenylene diacetate hydrolyzed readily when heated with 10% KOH on a water bath for 10 min. When the hydrolyzate was made acid or treated with CO_2, yellow crystals of 1,1'-dihydroxyferrocene precipitated; these crystals were extremely unstable in air. The 1,1'-dihydroxyferrocene was washed with water and dissolved in an alkaline solution, and benzoylation by the Schotten-Bauman method gave 1,1'-ferrocenylene dibenzoate.

Oxidation of 1,1'-dihydroxyferrocene. An ether solution of 1,1'-dihydroxyferrocene was prepared by hydrolysis of 0.80 g of 1,1'-ferrocenylene diacetate, and a stream of dry air was passed through the solution for 1.5 hr. The resulting brown precipitate was filtered and washed with ether. The precipitate was almost completely soluble in dilute HCl. The solution gave a reaction for Fe^{3+} with KCNS. The ether extract was washed with small amounts of water, 1% KOH, and again with water, and the ether was evaporated. The remaining crystals were sublimed under vacuum. There was obtained 0.06 g (14% of theoretical, calculated on the 1,1'-ferrocenylene diacetate used) of cyclopentadienone dimer, 4,7-methano-3a, 4,7,7a-tetrahydro-1,8-indenedione, with an m.p. of 96-98°. Literature values for the m.p.: 101-101.5°; 96-98° [6]. A mixture with a known sample melted without depression of the melting point.

1,1'-Ferrocenylene dibenzoate was prepared by benzoylation with benzoyl chloride (0.5 ml) of the hydrolyzate from the hydrolysis of 0.3 g of 1,1'-ferrocenylene diacetate in 6 ml of 10% KOH. The yield was 0.29 g (68% of theoretical); the m.p. was 108-110°; after recrystallization from alcohol the material melted at 114-115°.

Found %: C 67.65; 67.53; H 4.39; 4.49; Fe 12.88; 12.97
$C_{24}H_{18}FeO_4$. Calculated %: C 67.63; H 4.26; Fe 13.10

1,1'-Ferrocenylene dibenzenesulfonate was prepared from 0.3 g of 1,1'-ferrocenylene diacetate by hydrolysis and treatment with benzenesulfonyl chloride (0.5 ml). The yield was 0.36 g (72% of theoretical); the m.p. was 114.5-116.5°; after recrystallization from alcohol, the material melted at 119.5-120.5°.

*A. V. Gerasimenko aided in this experiment.

Found %: C 52.87; 52.92; H 3.68; 3.57; Fe 11.00; 11.23; S 12.53; 12.40

$C_{22}H_{18}FeO_6S_2$. Calculated %: C 53.02; H 3.64 Fe 11.21; S 12.87

1,1'-Dimethoxyferrocene was prepared in a manner similar to that by which methoxy ferrocene is prepared. To a solution of 0.70 g of 1,1'-ferrocenylene diacetate and 3 ml of dimethyl sulfate in 20 ml of absolute methanol was added dropwise 7.5 ml of 50% KOH. The mixture was refluxed for an hour; it was then diluted with water and extracted with ether. The ether extract was washed with water, and the ether was evaporated. There was obtained 0.54 g (95% of theoretical) of 1,1'-dimethoxyferrocene with an m.p. of 31.5-33°; after recrystallization from hexane solution saturated with 1,1'-dimethoxyferrocene at 30° and subsequently cooled with dry ice–acetone mixture, the material melted at 35-36°.

Found %: C 58.39; 58.58; H 5.87; 5.91; Fe 22.71; 22.47

$C_{12}H_{14}FeO_2$. Calculated %: C 58.55; H 5.73; Fe 22.70

O,O'-(1,1'-ferrocenylene)diglycolic acid. To the hydrolyzate obtained by hydrolysis of 0.50 g of 1,1'-ferrocenylene diacetate in 6 ml of 10% KOH was added a solution of 1.0 g of chloroacetic acid in 10% KOH. The mixture was refluxed for 3 hr, during which time the medium remained basic. The mixture was cooled and made acid, and the difficultly soluble potassium acid salt of the desired acid precipitated; this was filtered, washed with ether, and recrystallized from water.

Found %: C 45.46; 45.36; H 3.78; 3.77

$C_{14}H_{13}FeO_6K$. Calculated %: C 45.18; H 3.52

The material gave a reaction for potassium ion with sodium tetraphenylboron.

In order to obtain the free acid, the acid solution together with the precipitate was extracted with ether; the precipitate gradually disappeared, and the acid went into solution in the ether. The green, aqueous acid solution was reduced with sodium sulfite or thiosulfate, and the resulting solution was saturated with NaCl and extracted with ether. The combined ether extracts were washed with small amounts of water, the ether was evaporated, and the remaining crystals were dried over P_2O_5. There was obtained 0.42 g (76% of theoretical) of O,O'-(1,1'-ferrocenylene)diglycolic acid with an m.p. of 160-163°; after recrystallization from water and careful drying under vacuum over P_2O_5, the material melted at 168.5-169.5°.

Found %: C 50.53; 50.41; H 4.37; 4.30; Fe 16.91; 16.92

$C_{14}H_{14}FeO_6$. Calculated %: C 50.33; H 4.22; Fe 16.72

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CATALYTIC CONVERSION OF ALCOHOLS AND CYCLIC HYDROCARBONS OVER TITANIUM DIOXIDE

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In spite of the fact that titanium dioxide is reasonably available, it is among those catalysts which have not received a great deal of study. The object of the present work was to study the catalytic properties of TiO_2 prepared by different methods with respect to reactions of alcohols (ethyl, isopropyl, and n-propyl) and of hydrocarbons (cyclohexane, cyclohexene, and 1,4-cyclohexadiene); other objects were to investigate the kinetics of these reactions and to determine the energies of the bonds of C, H, and O atoms with the surface of the TiO_2. The differential thermocouple method was used to study these catalytic reactions, since this permitted us to circumvent a number of experimental difficulties. The 20-junction differential thermocouple (Chromel–Copel) differed from the one previously described [1-3] in that all junctions and the ordinary thermocouple were bonded to one half of a mica disc, the other half of which was left free. The distribution of the catalyst relative to the differential thermocouple is shown in Fig. 1. The e.m.f. of the differential thermocouple was continuously recorded by means of an ÉPP-09 potentiometer in which the zero position of the pointer was in the middle of the scale; this made it possible to determine both endothermic and exothermic heat effects of the various processes. A similar apparatus and experimental method have been described in reference [4]. The use of the differential thermocouple made it possible to study the change in catalyst activity over the course of each experiment, catalyst regeneration conditions, and carbon deposition processes.

TABLE 1

Change in the Composition of the Gaseous Products During the Course of an Experiment with Isopropyl Alcohol

Time from start of expt., min.	ΔH in scale divisions	Gas comp., vol. %	
		propylene	hydrogen
2—4	1—2	1,0	99,0
8—10	5—11	43,8	54,5
15—16	12—15	61,7	38,2
18—20	15—16	72,5	26,8
22—24	17—18	98,0	2,0

By means of the differential thermocouple in combination with chemical methods of analysis, it was established that in the case of isopropyl alcohol, the catalyst surface (of each of four samples) became covered with carbonaceous deposits in the first 15 to 20 min; associated with this was a sharp change in the ratio of dehydrogenation rate to dehydration rate. Conversion was practically confined to dehydrogenation during the first 2 to 5 min of the experiment; dehydrogenation and dehydration then occurred simultaneously, the ratio of the rates of these reactions decreasing, until 20 to 25 min after the beginning of the reaction practically only dehydration took place. However, the total amount of gas evolved per unit time remained constant over the course of the experiment. All of this shows that centers active for alcohol dehydrogenation become poisoned for this reaction during carbon deposition and simultaneously acquire the ability to dehydrate the alcohol at the same rate. The change

TABLE 2

Effect of the Method of Catalyst Preparation and of Carbon Deposition on the Catalytic Properties of TiO_2

Reaction	Condition of surface	Temp. interval, °C				ε, kcal / mole				K_0			
		sample No. 1	sample No. 2	sample No. 3	sample No. 4	sample No. 1	sample No. 2	sample No. 3	sample No. 4	sample No. 1	sample No. 2	sample No. 3	sample No. 4
Dehydrogenation of C_2H_5OH	p.c.	299—340	334—404	392—457	340—398	22,8	20,4	9,4	12,4	$1,0 \cdot 10^4$	$1,9 \cdot 10^5$	$1,4 \cdot 10^6$	$1,2 \cdot 10^4$
Dehydration of C_2H_5OH	p.c.	299—340	334—404	392—457	340—398	25,0	25,4	6,9	12,5	$1,5 \cdot 10^6$	$5,6 \cdot 10^6$	$3,7 \cdot 10^8$	$4,4 \cdot 10^4$
Hydrogenation of ethylene	p.c.	299—340	334—404	392—457	340—398	21,2	24,2	13,0	16,8	$1,8 \cdot 10^7$	$1,0 \cdot 10^8$	$1,3 \cdot 10^4$	$2,7 \cdot 10^5$
Dehydration of iso-C_3H_7OH	c.c.	221—255	253—316	294—324	293—303	22,9	9,1	26,2	17,2	$3,7 \cdot 10^8$	$9,1 \cdot 10^8$	$1,0 \cdot 10^{10}$	$2,8 \cdot 10^7$
Dehydrogenation of iso-C_3H_7OH	n.c.	266—310				11,9				$1,9 \cdot 10^5$			
Dehydrogenation of iso-C_3H_7OH	p.c.	266—310	253—304			9,1	10,4			$1,0 \cdot 10^4$	$2,2 \cdot 10^4$		
Dehydration of iso-C_3H_7OH	p.c.	266—310	253—304			24,4	15,3			$4,5 \cdot 10^8$	$6,9 \cdot 10^8$		
Dehydrogenation of C_6H_{12}	p.c.	443—486	460—523	480—518	454—505	19,0	14,7	21,6	15,0	$8,7 \cdot 10^8$	$5,1 \cdot 10^4$	$1,3 \cdot 10^4$	$3,5 \cdot 10^4$
Dehydrogenation of C_6H_{12}	c.c.	426—479				25,2				$4,9 \cdot 10^7$			
Dehydrogenation of C_6H_{12}	p.c.	403—460				25,0				$6,2 \cdot 10^7$			
Dehydrogenation of 1,4-C_6H_8	p.c.	362—456				22,3				$2,4 \cdot 10^7$			
Irreversible catalysis of C_6H_{12}	p.c.	300—425				26,1				$2,7 \cdot 10^8$			
Dehydrogenation of n-C_3H_7OH	p.c.	343—370				19,4				$2,3 \cdot 10^6$			
Dehydration of n-C_3H_7OH	p.c.	343—370				12,1				$4,5 \cdot 10^4$			

* p.c. - partially covered with carbon; c.c. - completely covered with carbon; n.c. - no carbon.

in the ratio of the rates of these two reactions was established by measuring the heat effect (in scale divisions of the ÉPP-09) over the first 15 to 20 min, and were confirmed by analyses of gas samples taken during the course of the experiment (Table 1).

Conditions for catalyst regeneration were determined by means of the differential thermocouple. After each experiment, the carbon film was removed in a strong current of air, the catalyst temperature first being raised to 40-50° above the experiment tenperature. Completion of regeneration was indicated by return of the pointer of the ÉPP-09 to the zero position. Regeneration usually required 20 to 30 min, the exact time depending on the conditions of the experiment. In order to obtain reproducible results for the purpose of calculating dehydrogenation and dehydration activation energies, the gaseous and liquid products from the conversion of isopropyl alcohol were collected at different temperatures and over time intervals corresponding to the same degree of carbon deposition. Times of equal carbon deposition were obtained from a graph showing the e.m.f. of the thermocouple as a function of time from the beginning of the experiment.

The effect of the method of TiO_2 preparation on catalyst activity was studied with four samples of TiO_2; these were prepared by precipitation of the hydroxide by treatment of $TiCl_4$ with water (No. 1), precipitation with ammonia (No. 2), air oxidation of freshly prepared $Ti(OH)_3$, which was precipitated by ammonia from $TiCl_3$ (No. 3), and hydrolysis of ethyl orthotitanate (No. 4). The hydroxide, $Ti(OH)_4$, was washed free of Cl^- ions, dried for 6 hr at 110°, and dehydrated by heating at a temperature which was continuously increased to 580° over a period of 24 hr. The catalysts were formed into pills having a diameter of 1 mm (No. 4 was used in the form of a powder). X-ray structural analysis of Sample No. 1 showed that it was anatase. Table 2 presents a list of the reactions which were studied over specific temperature intervals; also shown are values of the activation energies, K_0, and preexponential terms of the Arrhenius equation as well as the extent of coverage of the catalyst surface by carbon during the given reaction. Though data are presented for hydrogenation of ethylene, the reaction was not studied experimentally. In this connection, it may be mentioned that in all cases where the reactant was ethyl alcohol, a large amount of ethane was formed (up to 40%), and it is assumed that the latter was formed by hydrogenation of the ethylene over the TiO_2 catalyst [5, 6]. Upon examination of Table 2, it is seen that the method of catalyst preparation had a substantial effect on the values of ϵ and K_0 for each reaction.

The kinetics of the conversion of isopropyl alcohol and of cyclohexane were studied in detail with Sample No. 2. The relative adsorption coefficients, $\underline{z}$, of the reaction products were calculated from the dependence of reaction rate on composition for the following binary mixtures: alcohol–acetone and alcohol–hydrogen, alcohol–water and alcohol–propylene (dehydrogenation and dehydration of the alcohol), and cyclohexane–benzene and cyclohexane–hydrogen (dehydrogenation of cyclohexane); the calculations were carried out by means of the formula [7]:

$$z = \left(\frac{m_0}{m} - 1\right) \Big/ \left(\frac{100}{P} - 1\right),$$

where m_0 is the amount of reaction product formed (calculated in the vapor state under standard conditions) when the pure starting material was fed, and $\underline{m}$ is the amount formed when the feed consisted of a P mole percent mixture of the starting material and the reaction product for which $\underline{z}$ was being determined. Table 3

TABLE 3

Temperature Dependence of $\underline{z}$ and Values of ΔH^0, ΔS^0 and ΔF^0

Dehydrogenation of iso-C_3H_7OH				Dehydration of iso-C_3H_7OH			Dehydrogenation of C_6H_{12}		
t, °C	z_{H_2}	z_{acet}	$\Delta F°_{acet.}$, cal/mole	$z_{C_3H_6}$	z_{H_2O}	$\Delta F°_{H_2O}$, cal/mole	t, °C	$z_{C_6H_6}$	z_{H_2}
282	0,9	2,4	−1090,0		1,9	−707,0	444	0,6	0,7
294	0,9	1,7	− 665,0	0,2	1,4	−378,0	460	0,7	0,7
310	0,9	1,2	122,0	0,2	0,9	122,0	480	0,7	0,7

ΔH^0_{acet} = -23.1 kcal/mole; $\Delta H^0_{H_2O}$ = - 16.9 kcal./mole;
ΔS^0_{acet} = - 39.7 cal /degree /mole; $\Delta S^0_{H_2O}$ = 29.2 cal /degree/ mole.

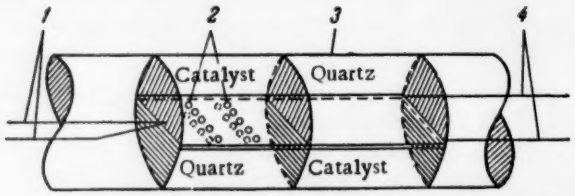

Fig. 1. 1) Ordinary Chromel–Copel thermocouple; 2) junction of Chromel–Copel differential thermocouple; 3) catalyst tube; 4) differential thermocouple leads.

TABLE 4

Bond Energies Calculated by the Kinetic Method

Bond TiO_2	Bond energy with TiO_2 sample			
	№ 1	№ 2	№ 3	№ 4
Q_{H-TiO_2}	57,1	60,5	53,1	57,1
Q_{O-TiO_2}	35,7	32,8	59,3	47,0
Q_{C-TiO_2}	20,7	20,3	23,0	23,4

presents the values of z at different temperatures for acetone, hydrogen, water, and propylene, as well as for benzene and hydrogen, which are products of the dehydrogenation of cyclohexane. Using the equations presented in references [8, 9], we were able to calculate from the temperature dependence of $z_{CH_3COCH_3}$ and z_{H_2O} the free energy change, ΔF^0, at constant P, the change in heat content ΔH^0, and the entropy change ΔS^0, for the adsorptive displacement of isopropyl alcohol from the active centers of the catalyst by acetone and water.

The data obtained allowed us to calculate, by the kinetic method [10, 11], the values of the bond energies Q_{C-TiO_2}, Q_{H-TiO_2}, and Q_{O-TiO_2} for each of the four samples of TiO_2 (Table 4).

Upon examination of Table 4, it may be seen that the method of catalyst preparation had an effect on the bond energies.

Thus, the present work represents the first detailed study of the kinetics of the dehydrogenation and dehydration of isopropyl alcohol and of the dehydrogenation of cyclohexane over titanium dioxide. The effect of the method of catalyst preparation on catalyst activity was investigated. This work also constitutes the first study of the ratio of the rates of the dehydrogenation and dehydration reactions. The values of the bond energies Q_{C-TiO_2}, Q_{H-TiO_2}, and Q_{O-TiO_2} were calculated.

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INHIBITION OF HYDROCARBON CRACKING IN THE PRESENCE OF MOLTEN POTASSIUM HYDROXIDE AND OF SODIUM

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Numerous molten or highly dispersed metals react with hydrocarbons and hydrocarbon radicals with the formation of organometallic compounds, and they also have a catalytic effect on the conversion of such compounds [1-12]. In this connection, it appeared to be of considerable interest to study in detail the reactions of hydrocarbons with various metals in their most reactive, i.e., molten state at high temperatures and under such conditions that free radicals are formed.

The conversion of n-heptane and cyclohexene in the presence of sodium and of potassium hydroxide at atmospheric and elevated pressures was studied in the present work, and this paper also presents for purposes of comparison the results of n-heptane cracking in the presence of molten aluminum. The pressure experiments were carried out in an autoclave, while those at atmospheric pressure were carried out in a flow apparatus. The n-heptane was continuously passed through a 150-mm layer of the molten metal or supported potassium hydroxide contained in the reactor. The contact time of the vapor with the packing was about 0.5 second at 700-800°. The potassium hydroxide was supported on KAD activated carbon. The reaction products were collected and analyzed.

Characteristics of the Starting Materials

Sodium: density 0.971, m.p. 97.7°, b.p. 880.9°. n-Heptane: b.p., 98°, d^{20}_4 0.6803, $n^{20}D$ 1.3960. Cyclohexene: b.p. 83-84°, d^{20}_4 0.8072, $n^{20}D$ 1.4480, iodine number 276. Potassium hydroxide: pure grade, catalog number 946. Technical grade aluminum with an aluminum content of 99.5-99.7% and an m.p. of 659.8° was used.

The data of Table 1 clearly show that sodium and potassium hydroxide have an inhibiting effect on the cracking of n-heptane, even at temperatures as high as 800°; in experiments with these materials, conversion was 5-7%, while in the absence of potassium hydroxide and sodium, the conversion was 34-57%.

On the other hand, aluminum caused considerable conversion of n-heptane, and the conversion increased with an increase in the temperature and residence time in the reaction zone; the conversion amounted to 65.3% at 700° and approached 100% at 800°, and it was almost twice as high as in experiments without aluminum.

The product gas from n-heptane cracking in the presence of sodium and KOH differed considerably in composition from the gas obtained from purely thermal cracking; the major part of the gas (60-85%) was hydrogen with a small amount of unsaturated hydrocarbons.

TABLE 1

Conditions and Material Balance for n-Heptane Cracking

Temp., °C	Feed rate, ml/hr	Yield, wt. %		Conversion, wt. %	Temp., °C	Feed rate, ml/hr	Yield, wt. %		Conversion, wt. %
		gas	condensate				gas	condensate	
Expt. with sodium					Expts. with activated KAD carbon				
200	68	no cracking or gas formation			600	107	5,7	91,8	9,7
300	57	0,1	94,2	0,1	700	105	11,5	86,6	17,9
450	71	1,8	80,3	1,8	800	102	23,7	73,5	34,7
500	51	2,5	75,1	2,5	Expts. with aluminum				
600	60	5,6	74,2	5,6					
700	83	6,8	74,0	6,8					
750	85	5,5	91,1	5,5	700	100	50,7	43,7	65,3
800	108	5,4	83,8	5,4	750	100	78,0	9,7	97,1
Expts. without sodium					800	100	72,5	12,3	99,5
					700	112	27,5	67,5	49,0
700	107	12,2	86,6	29,0	700	66	36,9	58,7	71,0
800	104	27,9	64,3	57,5	800	140	45,7	44,6	78,2
Expts. with potassium hydroxide supported on activated KAD carbon					800	86	77,3	14,0	100,0
					800	69	71,0	6,4	100,0
600	100	1,4	98,6	1,4					
700	99	3,9	96,1	3,9					
800	96	7,4	92,6	7,4					

TABLE 2

Composition of Product Gas from n-Heptane Cracking

Temp., °C	Gas comp., vol. %			Wt. of 1 liter of gas, g	Temp., °C	Gas comp., vol. %			Wt. of 1 liter of gas, g
	C_nH_{2n}	H_2	C_nH_{2n+2}			C_nH_{2n}	H_2	C_nH_{2n+2}	
Expts. with sodium					Expts. with potassium hydroxide supported on activated KAD carbon				
200	no gas formation				600	6,7	61,8	31,5	0,55
300	2,2	75,0	22,8	0,45	700	5,4	76,3	18,3	0,45
450	3,0	77,0	20,0	0,45	800	7,3	62,7	30,0	0,54
500	10,8	70,3	18,9	0,57	Expts. with activated KAD carbon				
600	7,3	78,5	14,2	0,30					
700	2,5	83,5	14,0	0,34					
750	1,0	84,6	14,4	0,25	600	22,9	47,9	29,2	0,82
800	0,5	83,6	15,9	0,27	700	22,5	43,1	34,4	0,74
Expts. without sodium					800	30,0	39,0	31,0	0,90
					Expts. with aluminum				
700	40,4	12,2	47,4	1,06					
800	44,0	22,5	34,0	0,993	700	50,2	15,3	84,5	1,17
					750	42,3	24,2	33,5	0,97
					800	36,2	30,5	33,3	0,85

Cracking of n-heptane in the presence of aluminum yielded gaseous and liquid reaction products characteristic of deep-seated pyrolysis. Condensation products, including carbenes, were also formed.

The condensate obtained from the cracking of n-heptane in the presence of sodium and of KOH consisted of unconverted n-heptane; i.e., no liquid reaction products were formed under these conditions.

It may be assumed that the initial stage of the reaction at 300-800° is the formation of organosodium compounds with the liberation of hydrogen, and that these compounds add at the instant of formation to

TABLE 3

Composition of the Gas from the Cracking of n-Heptane in Molten Sodium (in volume %)

Component	At 700°	At 800°	Component	At 700°	At 800°
Hydrogen	16,15	31,3	n-Butane	0,24	0,13
Methane	26,50	30,6	Butene + 1-butene	1,84	1,83
Ethane	8,95	5,8	2-Butene, cis and trans	0,58	0,14
Ethylene	31,15	21,91	2-Butene + C_4H_6, cis and trans	0,90	0,51
Propane	0,48	0,26	iso-Pentane + 3-methyl-1-butene	0,48	0,41
Propylene	11,15	6,5	n-Pentane	0,15	—
iso-Butane	0,34	—	1-Pentene	1,11	0,61

TABLE 4

Properties of the Condensate from the Cracking of n-Heptane

Temp., °C	Comp. by fractions, %			d_4^{20}	n_D^{20}	Iodine No.
	to 98°	98°	above 98°			
Original n-heptane	0	100	0	0,6803	1,3960	0
Expts. with sodium						
200	0	100	0	0,6808	1,3960	0
300	0	100	0	0,6870	1,3960	0
450	0	100	0	0,6811	1,3950	0
500	0	100	0	0,6825	1,3960	0
600	0	100	0	0,7000	1,4050	3,1
700	0	100	0	0,6846	1,3960	1,3
750	0	100	0	0,6820	1,3950	0,8
800	0	100	0	0,6803	1,3980	1,2
Expts. without sodium						
700	1,3	85,0	13,7	0,6863	1,3985	15,0
800	5,3	82,4	12,3	0,6882	1,3985	12,0
Expts. with potassium hydroxide supported on activated KAD carbon						
Original n-heptane	0	100	0	0,6859	1,3880	0
600	0	100	0	0,6854	1,3880	1,5
700	0	100	0	0,6853	1,3880	3,4
800	0	100	0	0,6859	1,3889	4,0
Expts. with activated KAD carbon						
600	1,0	98,5	0,5	0,6878	1,3890	4,2
700	2,2	96,8	0,6	0,6866	1,3880	11,0
800	3,3	96,0	0,7	0,6849	1,3880	14,0
In molten aluminum						
700	15,4	80,0	4,6	0,7031	1,4110	31,8
800	16,0	80,0	14,0	0,8535	1,5470	55,8

olefins, thereby inhibiting cracking, which is a chain process promoted by olefins.

$$C_7H_{16} + Na \rightarrow C_7H_{15}Na + H;\ C_nH_{2n} + 2H \rightarrow C_nH_{2n+2}$$

or

$$2C_7H_{16} + C_nH_{2n} + 2Na \rightarrow 2C_7H_{15}Na + C_nH_{2n+2}.$$

TABLE 5

Characteristics of Cyclohexene Conversion Products

Heating temp.	Iodine No.	n_D^{20}	d_4^{20}	Notes
Original cyclohexene	276	1,4480	0,8072	
400° with Na	274	1,4480	0,8097	Light, homogeneous
	278	1,4480	0,8122	Dark
500° with Na	203	1,4570	0,8192	Light, homogeneous
	74	1,4640	0,9103	Dark, tarry
500° with KOH	117	1,4475	0,8097	Light colored

Conversion of Cyclohexene

The experiments were carried out in an autoclave having a volume of 50 ml. The desired temperature of 400 or 500° was reached by gradual heating. The pressure increased to 20-70 atm, and these conditions were maintained for two hours; the heater was then switched off, and the autoclave was gradually cooled. The autoclave and electric furnace were mounted on a shaker, which provided agitation. At each temperature, experiments were carried out in the presence and in the absence of sodium.

At 500° and in the absence of sodium, cyclohexene was completely converted to a viscous, tarry product (sp. gr. 0.9103) with the formation of 2% gaseous products. There was little change in the presence of sodium; there was a decrease in iodine number, and about 1.4% gas was formed.

Thus, it has been shown for the first time that molten sodium and potassium hydroxide considerably inhibit the pyrolysis of n-heptane at 700-800° and atmospheric pressure, and also inhibit the condensation of cyclohexene at 500° under pressure in an autoclave, while molten aluminum accelerates the cracking of n-heptane at 700-800° and atmospheric pressure; i.e., cracking of n-heptane in a medium of molten aluminum takes place to a greater depth and produces 3-5 times more gas than when the reaction is carried out in the absence of aluminum.

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A NEW METHOD FOR THE SIMULTANEOUS DETERMINATION OF SILICON AND HALOGENS IN ORGANOSILICON COMPOUNDS

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In previous published work [1-4], it has been shown that reductive decomposition of organic substances by heating with metallic potassium in a hermetically sealed steel microbomb is effective and rapid. The effectiveness of this method is due to the fact that metallic potassium, which exists in the vapor state at 850-900°, provides for complete reduction of all of the elements occurring in an organic molecule. We have applied this reductive decomposition method to organosilicon compounds for the purpose of determining the silicon content. It is known that when inorganic silicon compounds are fused with metallic potassium, the silicon is reduced to elemental silicon [5], which is readily soluble in even weakly alkaline solutions with the formation of a soluble silicate.

In the present work, we have shown that this property of silicon can be put to use in analysis of organosilicon compounds. When organosilicon compounds are fused with potassium and the resulting mass is dissolved in water, potassium silicate is formed. The silicate can be determined by volumetric, colorimetric, and amperometric analysis [6-8].

Another important advantage of this method lies in the fact that volatile fluorine and silicon compounds are not formed during fusion of organic silicon compounds containing these elements; the formation of volatile compounds is characteristic of oxidative methods of decomposition. Consequently, simultaneous determination of silicon and fluorine is possible.

A sample of the material weighing from 5 to 15 mg is placed in the steel tube of a microbomb together with 25-100 mg of metallic potassium. The bomb is hermetically sealed and heated for 5 min in a furnace at 850-900°. The bomb is then cooled, and the resulting mass is dissolved in water. The solution is quantitatively transferred to a plastic beaker and allowed to stand for 10-15 minutes on a boiling water bath. After being cooled, the solution is transferred to a volumetric flask made of alkali-resistant glass, filtered from the carbon, and then divided into aliquot portions for the silicon determination.

Colorimetric determination of silicon. From 10 to 25 ml of the solution was placed in a 50-ml flask, the volume was brought to 35 ml by the addition of water, and 1 ml of 5 N H_2SO_4 and 3 ml of a 5% solution of ammonium molybdate were added. The solution was stirred and then allowed to stand for 10 min. Small portions of 8 N H_2SO_4 totalling 4 ml were then added to the flask. The solution was then diluted with water to a volume of 45 ml, and a drop of a 30% solution of $SnCl_2$ was added. Water was then added to bring the solution level

*Deceased.

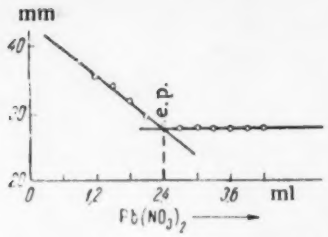

Fig. 1.

up to the calibration mark, and then, after a 5-min stirring, the color intensity was measured. The quantity of silicon (in mg) was determined from a graph.

Amperometric titration. A total of 5 to 25 ml of the solution was placed in the cell, and the volume was brought to 50 ml by the addition of 0.1 N KNO_3. The measurements were carried out under a continuous stream of nitrogen. The $Pb(NO_3)_2$ solution was added gradually from a buret, and the galvanometer readings were recorded over a period of 1.5 to 2 min. The equivalence point (e.p.) was determined graphically (Fig. 1). The results of colorimetric and amperometric analysis of pure substances are compared in Table 1.

TABLE 1

Colorimetric and Amperometric Determination of Silicon

Substance	Calc. Si, %	Colorimetric Si determination, %		Amperometric Si determination, %	
		found	diff.	found	diff.
Diethylsilanediol $C_4H_{12}OSi$	23,35	23,37 23,07	+0,02 −0,28	23,29 23,11	−0,06 −0,24
Triphenylethylsilane $C_{20}H_{20}Si$	8,67	8,50 8,87	−0,17 +0,20	8,60 8,52	−0,07 −0,15
Trimethylbutylsilane $C_7H_{18}Si$	21,73	21,50 21,32	−0,23 −0,41	21,67 21,68	−0,06 −0,05
Tetraethylsilane $C_8H_{20}Si$	19,44	19,57 19,23	+0,13 −0,21	19,33 19,35	−0,11 −0,09
1,4-Di(trimethylsilyl)benzene $C_{12}H_{22}Si_2$	25,22	24,50 25,01	+0,28 −0,21	25,20	−0,02

The acidimetric determination of silicon was based on the interaction of soluble silicates with fluorides in the presence of a specific amount of HCl with the formation of the fluosilicate K_2SiF_6 [6, 9, 10]. Table 2 presents the analytical results.

Simultaneous determination of silicon and halogens. The solution of the fused mass was brought to a predetermined volume and divided into several aliquot portions, thereby permitting determination of several elements with the same original sample. We determined silicon and halogens in the present case.

The determination of silicon by any of the methods indicated above was carried out on one aliquot sample, while another aliquot was used for the determination of chlorine, bromine, iodine, and fluorine. The Cl and Br were determined mercurimetrically, the I was determined iodometrically [1, 2], and the F was determined by thorium titration [3]. The experimental results are presented in Table 3.

We also analyzed γ-(α, α,β-trifluoro-β-chloroethoxy)propylmethyldichlorosilane. The percentage content of Si, F, and Cl were determined from one original sample.

Found %: Si 9.73; 9.73; F 19.75; 19.99; Cl 36.73; 36.72
Calculated %: Si 9.69; F 19.68; Cl 36.74

Thus, a new method for the determination of silicon has been developed. The method is based on the decomposition of organosilicon compounds by metallic potassium under reducing conditions. It has been shown that when silicon-containing organic substances are decomposed with metallic potassium in a hermetically sealed bomb at 850-900° and the resulting mass is dissolved in water, the silicon quantitatively goes into solution in the form of the soluble silicate K_2SiO_3. Amperometric titration has been applied to the determination

TABLE 2

Substance	Wt., mg	Si, %		
		calc.	found	diff.
Octamethyltetracyclosiloxane $C_8H_{24}O_4Si_4$	11,120 8,964	37,80	37,58 37,62	—0,22 —0,18
Hexamethyldiphenyltetracyclosiloxane $C_{18}H_{22}O_4Si_4$	18,615 13,521	26,66	26,82 26,61	+0,16 —0,05
Tetradiethylphenylsiloxytitanium $C_{40}H_{60}O_4Si_4Ti$	7,670 8,722	14,68	14,54 14,71	—0,14 +0,03
Trimethylhexylsilane $C_9H_{22}Si$	14,520 8,870	17,73	17,70 17,62	—0,03 —0,11

TABLE 3

Simultaneous Determination of Silicon and Halogens

Substance	Silicon, %			Halogen, %		
	calc.	found	diff.	calc.	found	diff.
Methylethyldichlorosilane $C_3H_8Cl_2Si$	19,58	19,60 19,57	+0,02 —0,01	49,48	49,53 49,40	+0,05 —0,08
1,5-Hexamethyl-2,3,4-trichlorophenyl-2,3,4-trimethylpentasiloxane $C_{27}H_{39}O_4Cl_3Si_5$	20,82	20,85 20,76	+0,03 —0,06	15,76	15,70 15,60	—0,06 —0,16
Bisiodomethyltetramethyldisiloxane $C_6H_{16}OI_2Si$	13,55	13,65 13,60	+0,10 +0,05	61,29	61,45 61,55	+0,14 +0,26
Diethylsilanediol + bromobenzoic acid	23,35	23,40 23,45	+0,05 +0,10	39,76	39,70 39,65	—0,06 —0,11
Diethylsilanediol + teflon	23,35	23,35 23,44	0,00 +0,09	76,00	76,20 75,90	+0,20 —0,10

of silicon in organic compounds. It has been established that it is possible to use the same sample for the determination of Si and halogens, including fluorine; the accuracy of the silicon determination is ± 0.2% when the amperometric method is used, ± 0.5% when the colorimetric method is used, and ± 0.3% when the volumetric method is used. The accuracy of the halogen determinations is ± 0.3%.

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THE ELECTRONIC STRUCTURE OF THE FERRICINIUM CATION AND OF OTHER AROMATIC METAL COMPLEXES

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In preceding work, we have calculated the molecular orbitals (m.o.) of a number of aromatic metal complexes: $(C_5H_5)_2Fe$, $(C_6H_6)_2Cr$, $(C_5H_5)_2Co^+$ and $(C_5H_5)_2Cr$ [1, 2]. In the present work, we used the same method and the same approximations to calculate the m.o. of the ferricinium cation. The m.o. types and their energies are shown in Table 1. In addition to those for $(C_5H_5)_2Fe^+$, the m.o. of the $(C_6H_6)_2Cr^+$ cation were also calculated, but in these calculations we were not able to make a satisfactory choice between the configurations

$$(a_{1g})^2 (a_{1u})^2 (e_{1g})^4 (e_{1u})^4 (e_{2g})^4 (a'_{1g})^1 \text{ and } \ldots (a'_{1g})^2 (e_{2g})^3;$$

however, we consider that the first is the more probable. Nevertheless, the resulting distribution of electron density was approximately the same for the two cases (a charge of + 1.4 atomic units on the Cr atom and -0.2 on each benzene ring), and the same is true of the energy of the upper occupied level, ~ 11-12 e.v., which determines the ionization potential of the cation (the second ionization potential of the dibenzenechromium molecule). We also attempted to carry out self-consistent calculations for $(C_5H_5)_2Co$ and $(C_2H_5)_2V$. In the first of these cases, we started with the results of our previous calculation of the m.o. of the cobalticinium cation, assuming that the spare electron in the neutral molecule occupies the lower free level of the cation (symmetry a''_{1g}), which consisted chiefly of the 4s orbital of Co. However, the resulting m.o. were not self-consistent, owing to the considerable difficulties associated with the fact that $(C_5H_5)_2Co$ is a radical with one unpaired electron which exists in an antibonding orbital. Therefore, we have been limited to evaluation of the effective charges. The greatest difficulties were encountered in the case of the vanadacene molecule, $(C_5H_5)_2V$, which contains three unpaired electrons, and here too we were able to establish only the electronic configuration of the molecule—. . . $(e_{2g})^2 (a'_{1g})^1$—and were limited to an evaluation of the effective charges.

TABLE 1

Molecular Orbitals of $(C_5H_5)_2Fe^+$ and Their Energies

Symmetry	Bonding m.o.		Antibonding m.o.	Symmetry	Bonding m.o.		Antibonding m.o.
	orbital type	energy, e.v.	energy, e.v.		orbital type	energy, e.v.	energy, e.v.
a_{1g}	$0,87a_{1g} + 0,49s$	—22,34	—7,78	e_{1u}	$0,80e_{1u} + 0,60p_x$	—18,83	—4,76
a'_{1g}	d_{z^2}	—15,92		e_{2g}	$0,35e_{2g} + 0,94d_{x^2-y^2}$	—15,18	—2,01
e_{1u}	$0,99a_{1u} + 0,09p_z$	—20,00	—6,45	e_{2u}	—	—	—3,00
e_{1g}	$0,89e_{1g} + 0,45d_{xz}$	—17,66	—1,60				

TABLE 2

Effective Charges in Aromatic Metal Complexes

Molecule	Effective charge			Molecule	Effective charge		
	on central atom	on both rings	on one ring		on central atom	on both rings	on one ring
$(C_5H_5)_2V$	~ +1,0	~ −1,0	~ −0,5	$(C_5H_5)_2Co$	~ +0,2	~ −0,2	~ −0,1
$(C_5H_5)_2Cr$	+1,7	−1,7	−0,85	$(C_5H_5)_2Co^+$	−0,1	+1,1	+0,55
$(C_5H_5)_2Fe$	+0,7	−0,7	−0,35	$(C_6H_6)_2Cr$	+1,5	−1,5	−0,75
$(C_5H_5)_2Fe^+$	+0,6	+0,4	+0,2	$(C_6H_6)_2Cr^+$	~ +1,4	~ −0,4	~ −0,2

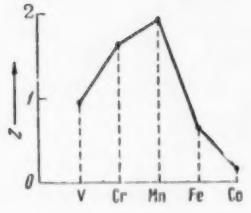

Table 2 presents the results of our calculations of the effective charges on the central atoms and on the rings of all of the molecules considered in the present and previous work.

The following conclusions may be formed from these results. The distribution of electron density in the cations, as compared to the corresponding neutral molecules, corresponds to the removal of an electron from the rings, since the effective charge of the neutral atom in all of the cations is close to the charge in neutral molecules.• The most reliable data are those on ferrocene (+ 0.7 charge on the Fe and −0.35 on each ring) and the ferricinium cation (+ 0.6 on the Fe and + 0.2 on each ring), and they are especially significant. These results are in agreement with experimental data showing that electrophilic substitution reactions are characteristic of ferrocene (with a negative charge on the rings), while in the case of the ferricinium cation, the characteristic reaction is nucleophilic substitution, and electrophilic substitution reactions do not take place (A. N. Nesmeyanov and É. G. Perevalova, unpublished work). According to our calculations, the positive charge in the $(C_6H_6)_2Cr^+$ cation is concentrated on the central atom, and the rings carry a small negative charge. This negative charge is significantly less than in dibenzenechromium, so that the transition from $(C_6H_6)_2Cr$ to the cation must be accompanied by a weakening of the tendency toward electrophilic substitution. As we have already indicated [1], the high electron density in the rings of ferrocene and dibenzenechromium is in agreement with the aromatic character of these complexes. The presence of a high π-electron density is apparent from the fact that ferrocene, like benzene, forms molecular compounds with electron acceptors [4]. It is interesting that the dibenzenechromium cation also forms a complex with $AlCl_3$ [5]. Apparently, although the electron density in the rings of the cation is low in comparison to the density in the rings of neutral dibenzenechromium, it is still greater than it is in, for example, the benzene molecule. We have previously remarked [3] that the cobalticinium cation with positive charges on the rings is inert in electrophilic substitution reactions. From the results obtained for the neutral cobalticene molecule, it follows that in this case both the central atom and the rings are electrically neutral, so that, in contrast to the cation, $(C_5H_5)_2Co$ should be capable of undergoing electrophilic substitution reactions, although possibly to a lesser extent than ferrocene.

The data presented in Table 2 show that for the neutral biscyclopentadienyl compounds, the effective positive charge (Z) on the central atom of the neutral molecules $(C_5H_5)_2M$ increases in the first part of the transition period, which is in agreement with the increase in ionic character on going from vanadicene to chromocene [6]. This tendency reaches its peak in the case of $(C_5H_5)_2Mn$, which, as is well known, is an ionic compound with a charge of + 2 on the central atom, as indicated by the presence of five unpaired electrons. Further addition of electrons leads to a sharp decrease in the ionic character in ferrocene and, in particular, cobalticene. It should also be noted that the effective charge on the V in $(C_5H_5)_2V$ is somewhat less than on the Fe in ferrocene, which is in agreement with the more ionic character of the first of these molecules [6]. The variation in the charges is illustrated in Fig. 1.

• This result was not obtained by simply considering the removal of an electron from the ring orbitals, but by a complete calculation in which we took into account the removal of an electron from the molecular orbital of the entire complex with subsequent self-consistency of the m.o. for the cation.

The results of our calculation of the self-consistent electronic configuration of the ferricinium cation shows that the ground valence state of Fe^+ should be $d_{z^2}^2 d_{x^2-y^2}^2 d_{xy} d_{xz} d_{yz}$ with an energy of the valence state of $4.5F_2 + 30F_4 + 6$ kcal for configurational excitation, i.e., a total of 33 kcal and not 58 kcal as we found earlier [7] upon the assumption that the ground valence state is $d_{z^2} d_{x^2-y^2}^2 d_{xy}^2 d_{xz} d_{yz}$. A similar ground valence state may be assumed for the ruthenocinium cation, the energy of which is about 18 kcal, according to our calculations, and this is 15 kcal less than that for ferricinium. On the other hand, as we have previously shown, the difference between the energies of the valence states of the central atoms in ferrocene and ruthenocene amounts to 75 kcal. Therefore, if ruthenocene is more stable than ferrocene as a consequence of the lower consumption of energy in excitation of the valence state, in the case of the ferricinium and ruthenocinium cations (where this difference is much less) a decrease in the difference in stability as compared to the difference in stability of the neutral molecules would be expected.

Note added in proof. A recent paper by Robertson and McConnel [9] reported magnetic moments for aromatic metal complexes. It follows from these data that these complexes can be divided into two groups: 1) those with purely spin values for the magnetic moments and 2) those having a magnetic moment greater than the spin value. The authors considered that the deviation of the magnetic moment of the molecule from its purely spin value is associated with unsymmetrical filling of m.o. of the type e_{2g} by electrons, which enter a.o. $3d_{\pm 2}$ instead. Under this assumption, the results of our calculations are in agreement with the experimental data for all of the compounds which we have considered. Moreover, Robertson and McConnel found that true orbital degeneration of the ground state can be encountered only in the ferricinium cation $Fe(C_5H_5)_2^+$, which is also in agreement with the results of our calculations.

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AN INVESTIGATION OF NEODYMIUM OXIDES BY ELECTRON DIFFRACTION

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There is no really complete description in the literature of the oxidation of neodymium. As a first approximation, it might be expected that neodymium and oxygen would form compounds similar in composition and structure to the oxides of cerium, praseodymium, and other rare earth metals. However, upon more detailed consideration, it appears that this is far from the case. It is known that all of the rare earth elements form sesquioxides – M_2O_3. As Yost et al. have indicated [1], the oxides of this composition are stable in air at room temperature. Among all of the rare earth elements, only cerium, praseodymium, and terbium form, at red heat, compounds with a greater oxygen content.

However, there are data to indicate that at room temperature, oxidation of Ce_2O_3 to CeO_2, of Tb_2O_3 to Tb_4O_7, and of Pr_2O_3 to Pr_6O_{11} takes place slowly, and that oxidation of Pr_2O_3 to PrO_2 takes place only when the sesquioxide is fused with sodium perchlorate [2].

With respect to the structural characteristics of the oxides of the rare earth elements and their changes upon heating in air, it is known that cerium, lanthanum, and praseodymium sesquioxides have hexagonal crystal lattices, and cerium and praseodymium dioxides (CeO_2 and PrO_2, respectively) have cubic lattices. Vickery [3] has established that the hexagonal modification of Pr_2O_3 transforms to the cubic form, and only the latter is converted to praseodymium dioxide by oxidation in air at high temperatures.

In contrast to these elements, terbium forms a cubic sesquioxide (Tb_2O_3), which is converted by further oxidation to TbO_2. It is now known that neodymium sesquioxide can exist in both the hexagonal and cubic modifications [4, 5].

Oxidation of neodymium to the higher oxide NdO_2 is still unknown. The literature contains no reports of the temperature conditions for the oxidation of neodymium, nor have intermediate oxides been reported. The present work was devoted to a study of the oxidation of neodymium; the method selected for this study was diffraction of fast electrons by thin films of neodymium oxide.

The evaporation of the neodymium and condensation of its vapors in films suitable for electron diffraction investigation was carried out in a special apparatus in which a vacuum of $6\text{-}7 \cdot 10^{-6}$ mm Hg was maintained. Since the rapidly moving neodymium atoms "burned through" the collodion film (the support), a copper screen (60-130 mesh), prepared electrolytically, was used to protect the film.

The very thin neodymium film thus obtained was placed in the electron diffraction camera, which had previously been prepared for the experiment, and an electron diffraction pattern of the as yet unoxidized neodymium was obtained immediately. A thermocouple was then sealed to the copper screen supporting the

TABLE 1

2r	I	d, Å	Neodymium		Nd_2O_3 cub.	
			I	d, Å	I	d, Å
13,3	1,00	3,16	0,25	3,15	1,00	3,199
15,2	0,30	2,76	1,00	2,79	0,30	2,76
17,2	0,05	2,45	0,20	2,46	0,05	2,47
21,8	0,60	1,92	—	—	0,60	1,95
25,5	0,30	1,64	0,20	1,67	0,30	1,67
33,9	0,10	1,23	0,10	1,15	—	—
38,0	0,10	1,10	0,10	1,15	—	—
40,0	0,05	1,05	0,10	1,08	—	—
46,1	0,05	0,930	—	—	—	—

neodymium film under investigation, and the film was heated in a furnace. The error in the measurement of the temperature of the screen did not exceed 10-15°. At the same time, separate pieces of the neodymium film were allowed to stand at room temperature in order to study the oxidation of neodymium in air.

The electron diffraction pattern obtained from the original neodymium film is shown in Fig. 1a. Data calculated from the pattern for $2L\lambda = 42.0$ are presented in Table 1. For identification of the phase composition of the sample, subsequent columns of the table contain values of the interplanar distances and intensities calculated by us from structural data [4, 5] for neodymium and the cubic modification of its sesquioxide.

Analysis of the intensities of the interference maximums and of the interplanar distances presented in Table 1 indicate a comparatively rapid oxidation of the thin neodymium film at room temperature and the formation of the cubic modification of the sesquioxide. We also investigated a number of other films prepared by evaporation and condensation of neodymium obtained from a 45% magnesium—neodymium alloy by sublimation of the magnesium under high vacuum. These films also proved to consist of neodymium and the same sesquioxide.

The electron diffraction study of films which had stood in air for two hours (one of the patterns is shown in Fig. 1 b) and for two days (Fig. 1c) established that even at room temperature, diffusion of oxygen into the film is quite rapid. In particular, this is indicated by the absence of rings characteristic of neodymium from the electron diffraction pattern shown in Fig. 1b. From calculations based on the pattern shown in Fig. 1b, it is clear that the compound formed had a cubic crystal lattice with the distance a = 11.21 A, which is somewhat greater than that indicated in reference [5] for the cubic modification of neodymium sesquioxide, for which the value a = 11.05 A was given.

It may be seen from the electron diffraction patterns of Fig. 1b and 1c that the compound formed gave interference rings which were diffuse. This indicates considerable distortion of the lattice.

In spite of the considerable scatter in the values of the lattice constants calculated from the different interference rings of Fig. 1c, the average value, a = 11.36 A, indicates a continuing increase of the dimensions of the unit cell of neodymium sesquioxide with an increase in the length of time during which the sample stood at room temperature.

TABLE 2

2r	I	d, Å	hkl	a, Å	2r	I	a, Å	hkl	a, Å
10,8	0,25	3,91	220	11,06	32,6	0,20	1,31	563	11,12
14,5	1,00	2,94	321	11,00	35,6	0,20	1,19	565	11,05
17,5	0,20	2,44	421	11,08	37,5	0,02	1,139	637	11,05
19,5	0,02	2,18	431 510	11,08	38,7	0,02	1,12	566	11,05
20,08	0,50	2,06	521	11,30	45,7	0,15	0,934	569	11,10
25,0	0,50	1,71	541	11,08	50,5	0,15	0,846	589	11,08
29,1	0,30	1,47	264	11,00					

These data and the significant diffusion of the diffraction pattern provide a basis for the assumption that under the conditions indicated, solution (diffusion) of oxygen in the lattice of the neodymium sesquioxide was prolonged, and this resulted in nonuniform distortion of the lattice.

From an analysis of the intensities of the interference rings and extinctions, it may be assumed that the lattice of the cubic neodymium sesquioxide belongs to one of the following space groups: P 23; $P2_13$; Pm 3; P $\bar{1}$3m; P $\bar{4}3_n$; P 43; P 4_23; P 4_33; $P4_13$; Pm3m; Pm 3_n.

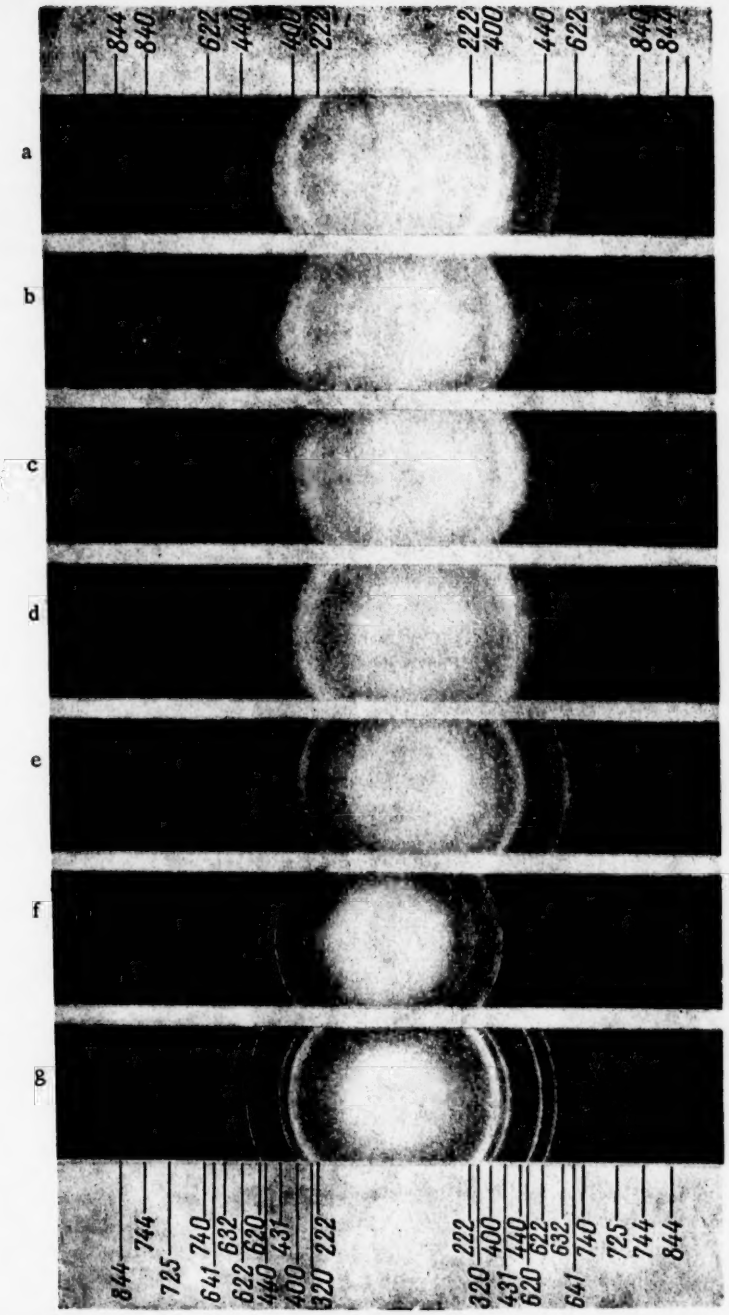

Fig. 1. Electron diffraction patterns of neodymium films: a) evaporated under vacuum; b) the same film after standing in air at room temperature for two hours; c) after standing in air at room temperature for two days; d) after heating in air at 500°; e) after heating in air at 700°; f) after heating in air at 900°; g) sprayed at 1800-1900° under a vacuum of 10^{-3} mm.

TABLE 3

hkl	d_{init}	d_{final}	Δd, A	Δa, A
222	3,16	3,28	0,12	0,415
400	2,76	2,89	0,13	0,520
440	1,92	1,98	0,06	0,340
622	1,64	1,72	0.08	0,530

An increase in the temperature at which the neodymium film was heated to 500° led to a substantial change in the structure of the film. A calculation based on the pattern shown in Fig. 1d established that the corresponding compound also had a cubic lattice with the constant a = 11.05 A. With a further increase in the temperature at which the sample was heated (to 700°), there was an increase in the intensity and sharpness of the interference rings of the corresponding electron diffraction pattern, which indicates an increase in the degree of order of the atoms in the crystal lattice. Data calculated from the electron diffraction pattern of this sample for $2L\lambda = 42.7$ are presented in Table 2.

The average value of the lattice constant is $a = 11.05 \pm 0.03$ A. In conformity with our analysis of the extinctions and indices of the reflecting planes, the compound could belong to one of the space groups enumerated above. In spite of the fact that the oxygen content of this compound was higher than that of the sesquioxide, the value obtained for the lattice constant of this compound was, nevertheless, the same as for cubic Nd_2O_3.

The reason that the volumes of the unit cells of these compounds containing specifically different amounts of oxygen were the same lies in the specificity with which the oxides of a number of elements, including the rare earth elements, form defect structures [6].

We made a number of approximate calculations for the purpose of estimating the compositions of the compounds formed under the conditions indicated above. The resulting data show that the change in the interplanar distances of the cubic modification of neodymium sesquioxide reaches significant values when the material is heated. These changes yield corresponding changes in the average values of the lattice constants.

Some of the data required for the approximate calculations mentioned above are shown in Table 3.

On the basis of the scatter of the values presented in Table 3, it may be assumed that the oxygen atoms were nonuniformly distributed throughout the crystal lattice. In our further calculations, we used the average value of the change in the lattice constant, $\Delta a = 0.451$ A.

Taking the diameter of the oxygen atom as 1.32 A and neglecting polarizability, compression, and other factors affecting the dimensions and state of the oxygen atoms introduced into the oxide lattice, we calculated the fraction of an oxygen introduced per unit cell of the oxide, assuming that the atoms are close packed.

The unit cell of Nd_2O_3 contains 1.5 oxygen atoms for each atom of neodymium. On the basis of the linear changes in the lattice of this compound (a basis which is not entirely justifiable), the maximum amount of oxygen introduced was (from the electron diffraction patterns):

$$\frac{\Delta a_{av.}}{2 at._{O_2}} = \frac{0,45}{1,32} \sim 0,34$$

atom per unit cell of Nd_2O_3.

Thus, at maximum saturation of the neodymium sesquioxide, the additional oxygen introduced at 700° was 1.84 atoms per atom of neodymium. From a calculation of the over-all amount of oxygen per neodymium atom, it is apparent that this amount of oxygen and neodymium corresponds to the compound Nd_6O_{11}. This result was confirmed by weighing the neodymium films before and after oxidation.

The new compound observed in the films heated at 500° apparently has the composition Nd_6O_{11}. It has a cubic lattice with the constant $a = 11.05 \pm 0.03$ A.

Investigation of the film heated at 900° indicated a further change in the diffraction pattern. A calculation based on the electron diffraction pattern shown in Fig. 1f indicated the presence of rings in addition to the somewhat weak rings corresponding to the assumed compound Nd_6O_{11}. These rings could be due either to the formation of a new phase with the constant a = 11.05 A or to distortion of the crystal lattice of the indicated compound, resulting in a transformation from the cubic to a tetragonal lattice with an axial ratio c/a close to 1. Such a distortion of the crystal lattice is quite probable, according to the Mikheev scheme of reversibility of structure during deformation [7].

When the temperature at which the films were heated was increased above 900°, the copper screen became unstable, and samples could not be prepared for investigation. In addition to the films discussed above, films prepared by spraying the neodymium at temperatures of 1800-1900° under a vacuum of 10^{-3} mm Hg were also studied by electron diffraction. The electron diffraction pattern of such a film is shown in Fig. 1g. The average value of the lattice constant as calculated from this electron diffraction pattern was 11.24 ± 0.03 A.

This value of the lattice constant is close to that reported in the literature [8] for cerium dioxide (CeO_2). This circumstance suggests that under the conditions indicated, the compound formed is probably NdO_2, the existence of which has not previously been known.

Thus, our investigation of the air oxidation of thin films of neodymium has shown that Nd_2O_3 and, probably, Nd_8O_{11} are formed at temperatures up to 700°. A compound apparently corresponding to NdO_2 was obtained only by oxidation of neodymium vapors. All of these compounds have cubic crystal lattices.

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THE INTERACTION OF N-BENZOYL-O-(BENZOYLPHENYLALANYL-C^{14})SERINE WITH RIBONUCLEASE

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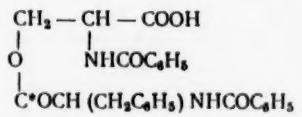
In a previous communication [1], we reported that N-benzoyl-O-(benzoylphenylalanyl-C^{14})serine



reacts with insulin and blood serum albumin in the presence of chymotrypsin with transfer of the benzoylphenylalanyl-C^{14} group to the albumin.

The present work was devoted to a similar investigation of ribonuclease. The reaction was carried out under the conditions used previously. The experimental data are presented in Table 1. As in our earlier experiments, treatment with a base did not remove the label from the albumin. However, in contrast to the behavior of other albumins, the addition of chymotrypsin to the reaction mixture did not activate the transfer of the benzoylphenylalanyl group to the albumin, and transfer was inhibited in the majority of cases. This observation led to the assumption that ribonuclease itself is capable of activating the process, while chymotrypsin is of the nature of an inhibitor for this reaction. This assumption was confirmed by the following experiments. In Expts. 10 and 10a (Table 1), chymotrypsin deactivated by boiling was used. As a result of this deactivation, the number of impulses per minute per 5 mg of albumin increased from 396 to 614-686. In Expts. 12, 13, and 14 (Table 2), ribonuclease deactivated by oxidation was used. There was almost no incorporation of the label when this ribonuclease was acted on by the O-peptide. When chymotrypsin was added to the mixture of oxidized ribonuclease and O-peptide, there was a sharp increase in labeling of the albumin (Expts. 12 and 13, Table 2).

Oxidation of the ribonuclease was carried out with performic acid [2]. Preparation "a" was precipitated with trichloroacetic acid, preparation "b" with acetone, and preparation "c" was lyophilized. Ribonuclease treated with urea was used in Expt. 15. According to the literature, urea has only an insignificant inactivating effect on ribonuclease [3], a fact which was reflected in our results. Ribonuclease which had been oxidized with performic acid completely lost its ability to react with the O-peptide, and the urea-treated material only partly reacted (Table 2). The question of the nature of the bond of the benzoylphenylalanyl group with the ribonuclease requires further investigation.

TABLE 1

Interaction of N-Benzoyl-O-(benzoylphenylalanyl-C^{14})serine with Ribonuclease

Expt. No.	Component ratio, O–N-peptide : albumin in moles	O–N-peptide, mg	Albumin, mg	Init. activity in test, imp/min*	Incorporation of label in imp/min per 5 mg of albumin		equiv O,N-peptide per g of albumin per hr	μ-equiv O,N-peptide per μ-equiv albumin**	Enzyme
					after TCA	after 0.1 N NaOH			
1		0,4	30	8 790	99	110	2,12	0,029	Chymotrypsin
2		0,4	30	15 688	130	98	1,08	0,014	»
1a	0,4 : 1	0,4	30	8 790	175	169	3,25	0,044	Without enxyme
2a		0,4	30	15 688	122	90	0,99	0,012	» »
3		1	30	17 760	230	67	1,63	0,022	Chymotrypsin
4		1	30	21 975	97	69	1,36	0,018	»
3a	1 : 1	1	30	17 760	263	110	2,67	0,036	Without enzyme
4a		1	30	21 975	375	430	8,47	0,10	» »
		1	30	39 222	410	334	3,69	0,05	» »
6		3	30	117 666	525	531	5,82	0,079	Chymotrypsin
6a	3 : 1	3	30	117 666	974	948	10,7	0,14	Without enzyme
7		5	30	196 110	250	283	3,13	0,042	Chymotrypsin
8		5	30	180 000	885	470	5,66	0,076	»
9		5	30	140 900	400	396	6,09	0,066	»
7a	5 : 1	5	30	196 110	1358	820	9,06	0,121	Without enzyme
7b		5	30	196 110	1004	888	9,82	0,131	» »
8a		5	30	180 000	845	638	7,69	0,104	» »
9a		5	30	140 900	538	492	7,56	0,082	» »
10		5	30	143 850	986	686	10,34	0,143	Chymotrypsin deactivated
10a		5	30	143 850	842	614	9,25	0,128	by boiling
11		5	30	124 250	485	359	6,25	0,081	Without enzyme

*The values cited take background into account.

**Ribonuclease molecular weight was 13,500.

TABLE 2

Incorporation of Label Into Oxidized and Urea-Treated Ribonuclease

Expt. No.	Treatment before incubation	Component ratio, O–N-peptide: albumin	Initial activity, imp per min	Incorporation of label				Enzyme
				in imp./min per 5 mg albumin per hr		equiv. of peptide per g of albumin	μequiv. of peptide per μequiv of albumin	
				after TCA	after NaOH			
12	Preparation "a", oxidized	5 : 1	180,000	302	254	2.77	0.037	Chymotrypsin
12a	Ribonuclease	5 : 1	180,000	28	22	0.24	0.003	Without enzyme
13	Preparation "b", oxidized	5 : 1	169,400	682	305	3.9	0.053	Chymotrypsin
13a	Ribonuclease	5 : 1	169,400	20	12	0.15	0.02	Without enzyme
14	Preparation "c", oxidized	5 : 1	140,900	34	20	0.308	0.004	" "
	Ribonuclease	5 : 1	140,900	39	18	0.277	0.0036	" "
		5 : 1	140,900	35	20	0.308	0.004	" "
15	Ribonuclease treated with urea	5 : 1	135,000	320	318	5.11	0.07	" "
		5 : 1	135,000	200	170	2.7	0.036	" "
		5 : 1	124,250	197	157	2.73	0.037	" "
		5 : 1	124,250	193	137	2.38	0.032	" "

EXPERIMENTAL

Crystalline ribonuclease (Vengriya) was used in these experiments. The preparation was electrophoretically homogeneous. Interaction of the ribonuclease with the O-peptide was carried out under the conditions used in our previous experiments [1]. The electrophoretic mobility of the preparation had not changed after incubation.

Oxidation of the ribonuclease. 1. Preparation "a" [2, 3]. To a solution of 80 mg of ribonuclease in 0.8 ml of 98% formic acid was added 0.02 ml of 30% H_2O_2. After 30 min, the albumin was precipitated by the addition of a tenfold volume of 10% trichloroacetic acid, the precipitate was centrifuged, washed with 5% trichloroacetic acid, an alcohol–ether mixture (1 : 3), and ether, and then dried.

2. Preparation "b" [2]. The oxidation was carried out in a manner similar to that described above. The albumin was precipitated with acetone, and the precipitate was centrifuged, washed with acetone, and dried.

3. Preparation "c" [3]. To 9 ml of 98% formic acid was added 0.45 ml of 30% H_2O_2; the mixture was allowed to stand for 1 hr at 20°, and was then cooled to 0°. Five ml of the cooled solution was added to 100 mg of the ribonuclease in 5 ml of formic acid. After the mixture had stood for 2 hr (cooled), a tenfold volume of water was added, and the mixture was lyophilized.

Treatment of the ribonuclease with urea [4]. Crystalline urea was added to the reaction mixture (O-peptide and ribonuclease) until the concentration reached 8 M, and incubation was carried out as before.

It has thus been shown that N-benzoyl-O-(benzoylphenylalanyl-C^{14})serine reacts with ribonuclease with transfer of the benzoylphenylalanyl group to the albumin. Chymotrypsin inhibits the reaction.

The authors take this opportunity to express their appreciation to M. G. Kritzman and A. S. Konnikova for assistance in this work and to M. A. Prokof'ev for the gift of the ribonuclease.

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•See C. B. translation.

A COLOR REACTION FOR HYDRAZINE AND SUBSTANCES WHICH YIELD HYDRAZINE

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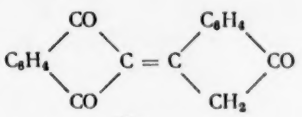
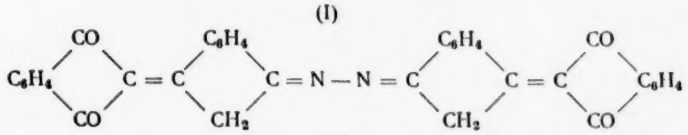
Several analytical color reactions for hydrazine are known: the reaction with dimethylaminobenzaldehyde [1], which is not very specific; the reaction with picryl chloride [2, 3]; and the reaction with salicylaldehyde [4], which yields a fluorescent product. The presence of hydroxylamine interferes with the determination of hydrazine by these reactions. The reaction with nitroindanedione is both sensitive and specific for hydrazine in the presence of hydroxylamine [5, 6]. In studying the interaction of other 1,3-indanedione derivatives with hydrazine, we found that anhydrobisindanedione, or bindone (I), is an even more characteristic reagent for hydrazine.

Bindone is already known as an analytical reagent for aliphatic and aromatic primary amines [7] and nitro compounds [8], and it is described in the most recent analytical manuals [9]. Bindone has recently found use in industry for the determination of small amounts of amines in the flotation of potassium salts [10, 11]. When bindone is heated with hydrazine hydrochloride in glacial acetic acid, the solution acquires a green color, and a dark green precipitate is formed. Judging from the analytical results and also by analogy with bindone derivatives, the precipitate is the azine of bindone (II). A more detailed description of the investigation of this material will appear in a separate communication.



(I)



(II)

The green color formed with bindone is very characteristic of hydrazine and its salts, and it may be used as a sensitive and specific reaction for hydrazine. The reaction is carried out by dissolving or suspending the substance to be investigated in glacial acetic acid; bindone is added as a solid (approximately 0.02-0.03 g of bindone for 3-4 ml of solution; excess bindone does not interfere with the reaction), and the mixture is heated for several minutes. When hydrazine is present, the solution acquires a green color, and a dark green precipitate is formed when the concentration is somewhat higher. The appearance of the green color with bindone in glacial acetic acid occurs down to a dilution of hydrazine hydrochloride of 1 : 100,000 or approximately 1 : 200,000 calculated on the basis of free hydrazine. When the concentration of hydrazine is very low, the solution is boiled for 3-5 min and then allowed to stand; the green color becomes noticeable after 20-30 min standing.

When it is desired to determine the presence of hydrazine in aqueous solutions, the solution is diluted with a four- or fivefold amount of glacial acetic acid, the bindone is added, and the mixture is boiled for 2-3 min and allowed to stand. The green color then appears. The sensitivity of the reaction in this case is less (1 : 20,000 with hydrazine hydrochloride). Hydrazine gives this green color with bindone in the presence of hydroxylamine. The latter forms a yellow monoxime with bindone [12], and this does not interfere with the detection of hydrazine. Even in the presence of a 1000-fold excess of hydroxylamine, hydrazine was detected at dilutions of down to 1 : 50,000 in the form of the hydrochloride or approximately 1 : 100,000 calculated as free hydrazine.

Since hydrazones and azines of aldehydes and ketones are rather readily cleaved by hydrochloric acid to yield hydrazine, they too can be detected with bindone. In this case, 0.02-0.03 g of bindone is added to the hydrazone in 3-4 ml of glacial acetic acid, the solution is heated to boiling, and 1-2 drops of concentrated hydrochloric acid are added. If a green color does not appear, the mixture is heated for 1 min. Acid hydrazides can be detected in a similar manner. Thus, for example, benzaldehyde was detected at dilutions down to 1 : 50,000, and benzoic acid hydrazide was detected down to 1 : 15,000.

There are indications in the literature that semicarbazones hydrolyze to hydrazine [13, 14]; therefore, they can be detected with bindone. But since the ease with which semicarbazones are hydrolyzed by hydrochloric acid differs with the particular semicarbazone, although the reaction with bindone is always positive, the specific dilution at which the green color is first observed varies considerably; thus, for example, the dilution is 1 : 25,000 for semicarbazide hydrochloride, 1 : 10,000 for acetone semicarbazone and cyclohexanone semicarbazone, and 1 : 250 for furacylene. Thiosemicarbazide (1 : 1000) and certain thiosemicarbazones also give a positive reaction.

Alkyl- and arylhydrazines (methyl-, ethyl-, phenyl-, acetylphenyl-, dinitrophenylhydrazines) do not give a positive reaction with bindone. The reaction is also negative with hydrazo- and azobenzene, diaminoguanidine, pyrazoline, aminopyrazoline, pyramidone, pyridazines, analgene, etc.

On the other hand, bindone derivatives do not give a green color with hydrazine; for example, methyl-, ethyl-, bromo-, dibromo-, bromomethyl-, bromoethyl-, and dinitrobindone give only a yellow color with hydrazine hydrochloride in glacial acetic acid. Only the methyl and ethyl ethers of the enol form of bindone give a positive reaction—a green color—but it appears that these substances are cleaved to bindone in glacial acetic acid.

Thus, hydrazine may be used, in turn, as a reagent for bindone. A little hydrazine hydrochloride is added to a solution of bindone in glacial acetic acid, and the solution is heated for 1 min; the green color appears either immediately or on standing. Bindone can be detected by this method in dilutions down to 1 : 10,000.

Bindone cannot be used as a reagent for hydrazine in the presence of primary amines, since primary amines give a violet or blue color with bindone in glacial acetic acid [7, 9]. In this case, preference must be given to 2-nitro-1,3-indanedione; although the reaction with this reagent is a little less sensitive, hydrazine can be detected in the presence of primary amines.

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C_5 DEHYDROCYCLIZATION OF ALKYLCYCLOPENTANES TO BICYCLIC HYDROCARBONS

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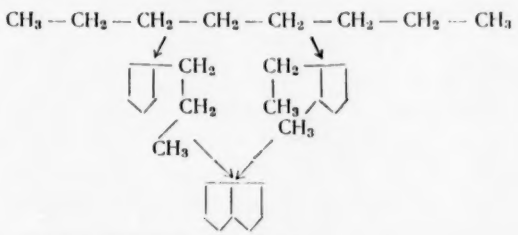
We recently published the results of a detailed investigation of the C_5 dehydrocyclization of n-octane in the presence of platinized carbon [1]. This work showed that n-octane cyclizes to yield the expected n-propyl- and 1-methyl-2-ethylpentanes in approximately equal amounts but in low over-all yield (2.2-4.5%). Moreover, it was noted that the catalyzate contained an additional product, which was also saturated. The catalyzate was freed from small amounts of unsaturates and aromatics and then distilled; the Raman spectrum of the residue from this distillation had an intense line at 762 cm^{-1}.• This line could not have been due to any paraffinic or cyclopentane hydrocarbon with eight carbon atoms in the molecule. It was proposed at that time that this line belonged to pentalane [bicyclo(3.3.0)octane], which could have been formed from the n-propyl- or 1-methyl-2-ethylcyclopentane as a result of a second C_5 dehydrocyclization:



This proposal was in agreement with the fact that catalyzates obtained in a similar manner from n-propylcyclopentane also had Raman spectra in which this line appeared. However, the spectra of cis- and trans-pentalanes were unknown, so that the proposal could not be confirmed without synthesis of these hydrocarbons. Since C_5 dehydrocyclization of paraffins or alkylcyclopentanes to bicyclic hydrocarbons had not previously been observed, we considered it desirable to carry out such a synthesis. This appeared to be of even greater interest, inasmuch as pentalane and methylpentalane were recently detected in petroleum [2], so that proof that the above reaction is basically possible would suggest possible routes for the formation of these compounds in petroleum.

In the present work, we were limited to the synthesis and to the study of the Raman spectrum of only one of the stereoisomeric pentalanes—the cis form. However, it turned out that this hydrocarbon was sufficient for our purpose, since not only the line at 764 cm^{-1}, but also several other previously unassigned lines in the spectrum of the fraction of the n-octane catalyzate mentioned above were found to be due to this compound. Thus,

•More accurate measurements gave 764 cm^{-1}.

the question of whether catalytic C_5 dehydrocyclization of paraffins and alkylcyclopentanes to pentalanes is possible must undoubtedly be answered affirmatively.

It is noteworthy that the yield of pentalane from n-octane was relatively high (0.25% of the catalyzate), despite the fact that it is a secondary product resulting from the conversion of cyclopentanes, which are themselves obtained in low yields. The pentalane yield was about 5%, calculated on the basis of the cyclopentanes formed. This appears especially significant when compared with the very low yield of pentalane obtained under comparable conditions from n-propylcyclopentane alone: ~ 1% at 310°; even at 320 and 330°, only about 1.5% pentalane was formed. One is inclined to suppose that the chief source of pentalane in the products from cyclization of n-octane is 1-methyl-2-ethylcyclopentane, which might well cyclize significantly more rapidly than n-propylcyclopentane.

EXPERIMENTAL

The cis-pentalane was prepared by a route similar to that developed by Vossen [3], and it was purified in a column having an efficiency of 100 theoretical plates. It had the following properties: b.p. 138.5°/760 mm; $n^{20}D$ 1.4625; d^{20}_4 0.8693. The literature reports essentially the same values [4]: b.p. 136°/755 mm; $n^{18}D$ 1.4629; d^{18}_4 0.8718.

The spectrum of the cis-pentalane was obtained and measured by methods previously described in reference [5].

$\Delta\nu$ (cm^{-1}): 194(6, b), 288 (2), 313 (0), 334 (1), 352 (1), 388 (9), 432 (1), 470 (1), 513 (5), 532 (8), 541 (8), 585 (12), 600 (2), 617 (2), 638 (1), 727 (2), 764 (100), 815 (1), 828 (20), 856 (3), 874 (5, b), 900 (74), 912 (15), 946 (12), 1009 (35), 1034 (23), 1050 (30), 1073 (2), 1126 (10), 1169 (12), 1187 (10), 1223 (15), 1249 (3,b), 1275 (6), 1294 (10), 1310 (18), 1335 (5), 1447 (76, b), 1474 (15), 2859 (320), 2901 (200, b), 2922 (100 bg), 2937 (350, bg) 2954 (450, bg).*

Content of pentalane in the n-octane catalyzate. The residue (from the distillation of the catalyzate), which had been obtained earlier [1], was quantitatively analyzed by means of its Raman spectrum [6]. Found: n-octane, 30%; n-propylcyclopentane, 55%; and cis-pentalane, 15%. When recalculated on the basis of the total catalyzate, the yield of pentalane from n-octane amounted to 0.25%, since the residue comprised 1.7% of the catalyzate.

Cyclization of n-propylcyclopentane to pentalane. The n-propylcyclopentane, which was redistilled in a column having an efficiency of 100 theoretical plates, had a b.p. of 130.9°/760 mm; and $n^{20}D$ 1.4264 and d^{20}_4 0.7765. It was passed over platinized carbon at a space rate of 0.2 $hours^{-1}$ and at temperatures of 310, 320, and 330°. Each experiment was carried out over a freshly prepared portion of catalyst. The content of unsaturates

TABLE 1

Results of Experiments on the C_5 Dehydrocyclization of n-Propylcyclopentane to Pentalane

Expt. No.	Temp., °C	Amt. n-propylcyclopentane charged, g	Catalyzate obtained, g	$n^{20}D$ of catalyzate before and after chromatography		Unsaturates content by Br No., %	Aromatics content, %	Charged to distillation, g	Residue, g	$n^{20}D$ of residue	Pentalane yield, %
				before	after						
1	310	30,8	28,4	1,4261	1,4257	2,7	~0,2	18,0	2,15	1,4293	~1
2	320	39,3	33,4	1,4272	1,4263	Not determined		29,7	3,2	1,4314	~1,5
3	330	38,7	37,4	1,4274	1,4262	6,9	~0,4	32,5	3,4	1,4303	~1,5

was determined by bromine number, and the aromatics content was determined by measuring the index of refraction before and after chromatographing over silica gel (taking the unsaturates into account). The chromatographed catalyzate was then distilled in a column having an efficiency of 50 theoretical plates in order to remove the

*"bg" indicates a line located against a background of considerable intensity—Publisher's note.

greater part of the unreacted n-propylcyclopentane and its hydrogenolysis products—paraffinic hydrocarbons; the amount of cis-pentalane in the residue was determined by refractive index. The presence of the line at 762 cm^{-1} in the spectra of such residues was shown previously [1]; this line is characteristic of cis-pentalane. The results of these experiments are presented in Table 1.

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SYNTHESIS AND CONVERSIONS OF MONOCYCLIC SECONDARY ACETYLENIC ALCOHOLS

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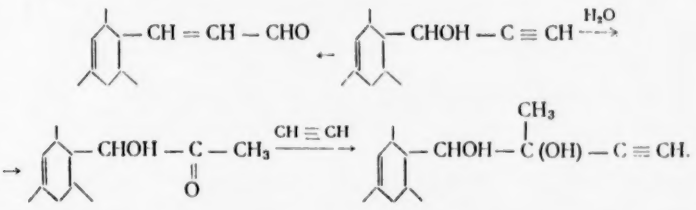
The subject of the present investigation comprised secondary acetylenic alcohols of the type of I-VII, which were synthesized from acetylene and Δ^3-cyclohexene aldehydes VIII-XV, the latter being easily obtained by condensation of readily available dienes and dienophiles. We used these alcohols to form cycloaliphatic polyene systems having a structure closely similar to naturally occurring structures. These systems were synthesized by hydration of the acetylenic bond of the alcohol with conversion to the ketol and then to the tertiary acetylenic glycol or by isomerization of the secondary acetylenic alcohols to α,β-unsaturated aldehydes and ketones with subsequent growth of the polyene side chain:

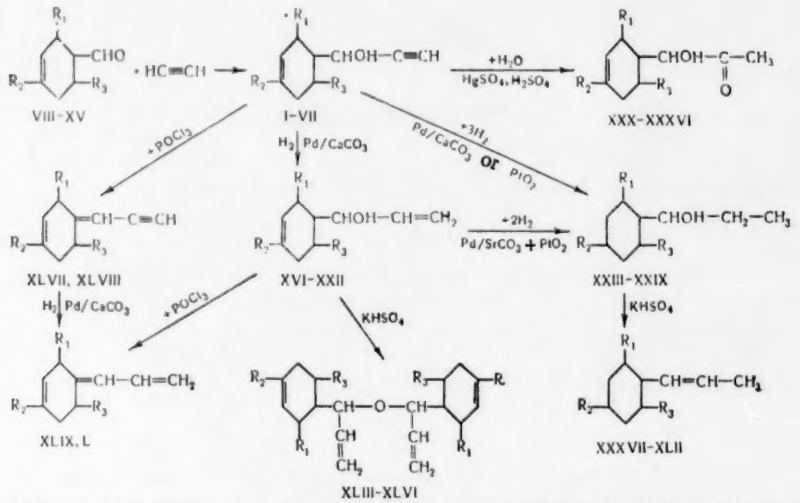


The scarcity of information on secondary acetylenic alcohols [1-6], and the absence of any data on the properties of acetylenic alcohols of the series selected for the present work, made it necessary to carry out a detailed and systematic investigation of the reactivity of such alcohols. That we had available such alcohols with different numbers of substituents differing in character and position in the Δ^3-cyclohexene ring made it possible to trace the effect of structural factors on the properties of the alcohols themselves as well as on the intermediate compounds obtained in the later stages of synthesis of the polyene systems.

The alcohols I-VII were synthesized from acetylene and the appropriate Δ^3-cyclohexene aldehydes, VIII-XV, in the presence of sodium in liquid ammonia at temperatures of from -40 to -70°.• The original aldehydes, VIII-XV, were prepared by Diels-Alder condensation of acrolein, crotonaldehyde, and cinnamaldehyde with butadiene, piperylene, 2-methylbutadiene, and 1-phenylbutadiene; the condensation was carried out at 160-200° in a metal tube in the presence of hydroquinone. The yields of monocyclic secondary acetylenic alcohols were 30-60%, and they depended to a great extent on the structure of the aldehyde used. Thus, the para substituted Δ^3-cyclohexenal XII reacted readily with acetylene, while the ortho substituted cyclohexenals IX,

•It was necessary to carry out the reaction in dimethoxymethane (and not in ether), which brought about a significant decrease in the formation of nitrogen-containing products.

X, and XI entered into the reaction with difficulty, and there was almost no reaction of the phenyl substituted aldehyde XV with acetylene under comparable conditions. However, the effect of the nature and position of the substituents was almost undetectable in the hydrogenated analogs of the Δ^3-cyclohexene aldehydes—they all very readily formed secondary acetylenic alcohols, and the yields were good.



I, VIII, XVI, XXIII, XXX, XXXVII, XLIII, XLVII, XLIX: $R_1=R_2=R_3=H$
II, IX, XVII, XXIV, XXXI, XXXVIII, XLIV: $R_1=CH_3$; $R_2=R_3=H$
III, X, XVIII, XXV, XXXII, XXXIX: $R_1=C_6H_5$; $R_2=R_3=H$
IV, XI, XIX, XXVI, XXXIII, XL: $R_1=R_3=CH_3$; $R_2=H$
V, XII, XX, XXVII, XXXIV, XLI, XLV: $R_1=R_3=H$; $R_2=CH_3$
VI, XIII, XXI, XXVIII, XXXV: $R_1=H$; $R_2=R_3=CH_3$
VII, XIV, XXII, XXIX, XXXVI, XLII, XLVI, XLVIII, L: $R_1=R_2=H$; $R_3=CH_3$
XV: $R_1=CH_3$; $R_2=H$; $R_3=C_6H_5$

The acetylenic alcohols were selectively hydrogenated over Lindlar catalyst or with one mole of hydrogen and palladium catalyst to the corresponding ethylenic alcohols XVI-XXII. Exhaustive hydrogenation of acetylenic alcohols I-VII and of ethylenic alcohols XVI-XXII was easily accomplished over $Pd/CaCO_3$ or PtO_2, and led to their saturated analogs XXIII-XXIX.

The secondary acetylenic alcohols I-VII were hydrated in the presence of mercurous sulfate and sulfuric acid to the corresponding hydroxyketones XXX-XXXVI. During the hydration of these alcohols, it was noted that hydration of acetylenic alcohols II and III does not occur, and the alcohols were recovered unchanged; however, when the experiment was repeated using the alcohols recovered from the reaction mixture, the corresponding ketols XXXI and XXXII were formed.

The saturated alcohols XXIII, XXIV, XXV, XXVI, XXVII, and XXIX were rather easily dehydrated, giving the ethylenic hydrocarbons XXXVII-XLII in quantitative yields, by heating with potassium bisulfate at 160-190°. Dehydration of the secondary ethylenic alcohols under the same conditions followed a different course; alcohols XVI, XVII, XX, and XXII gave good yields of ethers XLIII-XLVI. The secondary acetylenic alcohols I-VII were not changed under the indicated dehydration conditions in the presence of potassium bisulfate. When the dehydration was carried out in pyridine in the presence of phosphoryl chloride and under an atmosphere of nitrogen, the corresponding hydrocarbons were obtained. From the analytically pure hydrocarbons were isolated hydrocarbons XLVII and XLVIII, which, according to infrared spectroscopy, were vinylacetylenic hydrocarbons with conjugated multiple bonds.* Dehydration of the secondary ethylenic alcohols XVI and XXII under the influence

*The acetylenic bond frequency (2137 cm^{-1}) was more intense and was lower by 20 cm^{-1} than that of the original alcohols, and in the region for double bond absorption there were two frequencies: 1654 cm^{-1}, which is characteristic of a double bond in a ring, and 1635 cm^{-1}, which was more intense than the first. From the shift in the frequency characteristic of acetylenic bonds and from the intensity of the band at 1635 cm^{-1}, it may be stated that the acetylenic and ethylenic bonds in the molecules of hydrocarbons XLVII and XLVIII are conjugated.

	Yield, %	B.p., °C/mm	$n^{20}D$	d^{20}_4	Calculated, %		Found, %	
					C	H	C	H
I	54	83—85/3	1,5032	0,9818	79,11	8,82	79,53	9,12
II	40	84/2,5	1,4990	—	80,00	9,33	80,00	9,44
III	26	139—140/1	1,5657	—	84,82	7,60	84,73	7,85
IV	50	89/3	1,4970	0,9869	80,48	9,73	79,88	9,98
V	53	88—90/2	1,5005	1,9804	80,00	9,33	79,76	9,22
VI	45	99—101/4	1,4980	0,9805	80,48	9,75	80,30	9,95
VII	60	77—78/1	1,4988	0,9827	80,00	9,33	80,20	9,29
XVI		89—91/6	1,4940	0,9591	78,26	10,14	78,19	10,40
XVII	80	78/4	1,4905	0,9826	78,95	10,52	78,62	10,30
XVIII	83	151/4	1,5804	1,0502	84,03	8,46	83,8	8,46
XIX	83	92/4	1,4968	0,9590	79,51	10,84	79,35	11,09
XX		88—89/5	1,4845	0,9480	78,95	10,52	78,86	10,52
XXI		98/5	1,4787	0,9475	79,51	10,84	79,51	10,96
XXII	80	71—72/1	1,4920	0,9555	78,94	10,52	79,09	10,50
XXIII		82—84/5	1,4625	0,9140	76,05	12,67	75,89	12,60
XXIV	80	55/0,4	1,4655	0,9177	76,92	12,82	76,33	12,6
XXV	86	134/0,5	1,5320	1,0102	82,54	10,16	82,58	9,99
XXVI	85	68,5/2	1,4681	0,9130	77,64	12,94	77,39	12,89
XXVII		87—89/6	1,4575	0,8990	76,92	12,82	76,87	12,51
XXX	24	95—96/3	1,4965	1,0644	70,13	9,09	70,04	9,00
XXXI		95—97/2,5	1,4898	1,0234	71,42	9,52	70,03	9,70
XXXII	50	141—142/0,4	1,4490	1,1058	78,25	7,87	78,04	7,90
XXXIII	66	90/1,5	1,4915	1,0105	72,52	9,89	72,62	10,09
XXXIV	25	100—101/2,5	1,4990	1,0470	71,43	9,52	71,32	9,52
XXXV	35	120—122/10	1,4951	1,0233	72,52	9,89	72,48	10,34
XXXVI		89/1	1,4870	—	71,43	9,52	71,35	9,68
XXXVII	70	65—66/15	1,4552	—	87,10	12,90	87,21	12,82
XXXIX	67	93,5—94/1	1,5990	0,9418	89,99	10,10	90,00	10,00
XLI		79—82/26	1,4715	—	86,90	13,04	86,70	13,20
XLII		63—64/13	1,4560	—	86,90	13,04	86,67	12,90
XLIII	80	156—157/1,5	1,5094	0,9568	83,72	10,07	83,67	10,24
XLIV		138/0,3	1,5057	—	83,91	10,49	83,51	10,70
XLV		165—166/3	1,5190	—	83,91	10,49	84,13	10,01
XLVI	80	160—161/1	1,5017	0,9495	83,91	10,49	83,88	10,66
XLVII	20	75—76/14	1,5184	0,9332	91,52	8,47	91,20	8,32
XLVIII	26	84/17	1,5170	0,9251	90,91	9,09	90,74	9,11
XLIX	18	65—67/15	1,5075	0,8920	90,00	10,00	89,74	10,23
L	25	75/17	1,5055	0,8820	89,55	10,45	89,32	10,44

of phosphoryl chloride led to the formation of hydrocarbons XLIX and L with conjugated ethylenic bonds; the infrared spectra of these hydrocarbons had an intense band at 1602 cm^{-1}, which indicates conjugation of the multiple bonds in the molecules. The diethylenic hydrocarbons XLIX and L were prepared by selective hydrogenation of hydrocarbons XLVII and XLVIII. It should be noted that in a number of cases separation of the products from the reaction mixture after dehydration with $POCl_3$ was considerably impeded by tar formation and the presence of chlorine-containing products. Therefore, it was not possible to prepare analytically pure dehydration products from ethylenic alcohols XVII-XXI and acetylenic alcohols II-VI [dehydration of these alcohols in the vapor phase in the presence of P_2O_5 or $Al_2(SO_4)_3$ was accompanied by tar formation].

Properties of the compounds synthesized in the present work are shown in the table. All of the saturated, ethylenic, and acetylenic alcohols were also characterized as the acetates.

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SAPONIFICATION OF TETRAETHYLACETALS OF β-DICARBONYL COMPOUNDS AND SOME SYNTHESES EMPLOYING THE RESULTING COMPOUNDS

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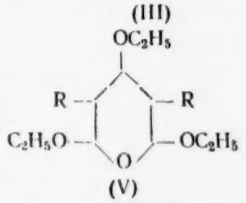
In previous work [1, 2], we developed general methods for the synthesis of tetraethylacetals of β-dicarbonyl compounds of the type $(C_2H_5O)_2CHCHRCH(OC_2H_5)_2$ and $RC(OC_2H_5)_2CH_2CH(OC_2H_5)_2$ and tetraethylacetals of ethoxydialdehydes of the type $(C_2H_5O)_2CHCHR[CH(OC_2H_5)CHR]_n CH(OC_2H_5)_2$, where n is 1, 2, or 3. In order to be able to use such compounds for purposes of synthesis, it was necessary to develop methods for their conversion to the corresponding carbonyl compounds.

It was found that saponification of the tetraethylacetals (I) by a single equivalent of water [3] in the presence of p-toluenesulfonic acid is a general method for the synthesis of β-formylvinyl ethers (II), further saponification of which led to substituted malonaldehydes (III). These results are in agreement with those of Isler [4], who used this route to obtain β-formyl-β-methylvinyl ethyl ether, which he successfully used for the synthesis of 15,15'-dehydro-β-apo-12'-carotenal and similar compounds. The i.r. spectrum of our β-formylvinyl ethers contained an absorption band in the region of 1675 cm^{-1}, which confirmed that they are α,β-unsaturated aldehydes. However, in addition to this band, the i.r. spectra of these compounds also contained a weak absorption band at 1734 cm^{-1}, which indicates the presence of a small amount of saturated aldehydes as impurities.

The saponification of the tetraethylacetal of β-ethoxyglutaraldehyde (IV) by one equivalent of water was accompanied by cyclization, and the major product of the reaction was 2,4,6-triethoxytetrahydropyran (V). The i.r. spectra of the triethoxytetrahydropyrans prepared in this manner contained no absorption bands characteristic of the CO group, which is quite unequivocal confirmation of their structure. It was established previously [2] that saponification of ethoxytetraethylacetals of the type of (VI) with an excess of water led to the corresponding ethoxydialdehydes (VII), which were the only compounds obtained in good yield.

$$(C_2H_5O)_2CHCH(R)CH(OC_2H_5)_2 \xrightarrow{H_2O} C_2H_5OCH=C(R)CHO \rightarrow HOCCH(R)CHO$$
(I) R = H, CH_3, n-C_5H_{11} (II) (III)

$$(C_2H_5O)_2CHCH(R)CH(OC_2H_5)CH(R)CH(OC_2H_5)_2 \xrightarrow{H_2O}$$
(IV) R = H, CH_3



(V)

$$(C_2H_5O)_2CHCH(R)[CH(OC_2H_5)CH(R)]_nCH(OC_2H_5)_2 \xrightarrow{H_2O} HOCCH(R)[CH(OC_2H_5)CH(R)]_nCHO$$
(VI) n = 1, 2, 3; R = H, CH_3 (VII)

$$RC(OC_2H_5)_2CH_2CH(OC_2H_5)_2 \xrightarrow{H_2O} RCOCH_2CH(OC_2H_5)_2 \qquad R = CH_3,\ C_2H_5,\ C_4H_9,\ C_6H_5$$
(VIII) (IX)

The saponification by a single equivalent of water of the tetraethylacetal of acetoacetaldehyde and its derivatives (VIII) proceeded in a peculiar manner; only diacetals of the type of (IX) were formed in good yield in this case. None of the compounds obtained in this manner gave a positive Fehling reaction, and their i.r. spectra had an intense absorption band at 1717 cm^{-1}, which is characteristic of a free ketone group and thereby confirms their structure.

With the aim of using the compounds described above in syntheses, some of their reactions at the aldehyde and ketone groups were studied. It was found that dialdehydes of the type of (III) and (VII) readily react with carboethoxymethylenetriphenylphosphorane (X) under the conditions of the Wittig reaction, forming the corresponding diethyl esters of unsaturated dicarboxylic acids (XI) and (XII) in high yields. The various β-formylvinyl esters are also capable of undergoing this reaction. For example, β-formyl-β-methylvinyl benzoate (XIII) reacted with phosphorane (X) to give 1-carboethoxy-4-methyl-5-benzoyloxy-2,4-pentadiene (XIV), from which the 2,4-dinitrophenylhydrazone of the corresponding formyl ester (XV) was prepared:

$$HOC-CHR-CHO \xrightarrow[(X)]{(C_6H_5)_3P=CHCOOC_2H_5} C_2H_5OOCCH=CHCHRCH=CHCOOC_2H_5$$

(III) R = H, CH_3, n-C_5H_{11} (XI)

$$HOC-CHR[CH(OC_2H_5)CHR]_nCHO \rightarrow$$

(XII) R = H, CH_3, n = 1, 2, 3

$$\rightarrow C_2H_5OOCCH=CHCHR[CH(OC_2H_5)CHR]_nCH=CHCOOC_2H_5$$

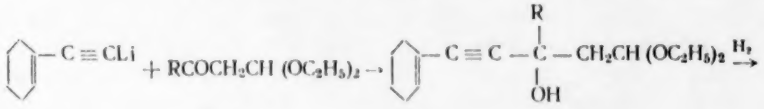
$$C_6H_5COOCH=C(CH_3)CHO \rightarrow$$

(XIII)

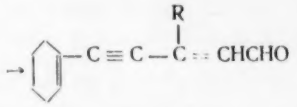
$$\rightarrow C_6H_5COOCH=C(CH_3)CH=CHCOOC_2H_5 \rightarrow HOCCH(CH_3)CH=CHCOOC_2H_5$$

(XIV) (XV)

The β-ketoacetals (IX) do not react with carboethoxymethylenetriphenylphosphorane. However, they readily undergo acetylene synthesis with lithium cyclohexen-1-ylacetylide giving good yields of acetylenic alcohols of the type of (XVI), saponification and dehydration of which yields the unsaturated aldehydes (XVII).



(IX) (XVI)



(XVII)

All of the conversions described above open up broad possibilities for the synthesis of different polyene compounds related to natural substances, and this will be the subject of our investigations of the near future.

EXPERIMENTAL

Hydrolysis of the tetraethylacetal of malonaldehyde. A mixture of 44 g of the tetraethylacetal of malonaldehyde and 3.8 g of a solution of p-toluenesulfonic acid containing 5.4 g of the acid and 180 g of water was stirred while heating on a water bath until a homogeneous solution was formed and then for an additional hour. The mixture was cooled, and 4 g of powdered sodium bicarbonate was added; the mixture was stirred for an hour, filtered, and distilled twice. There was obtained 11.8 g of β-formylvinyl ethyl ether with a b.p. of 77-81° at 14 mm and 54-55° at 5 mm; $n^{20.5}D$ 1.4472.

Found %: C 59.40; 59.33; H 8.74; 8.76

$C_5H_8O_2$. Calculated %: C 59.98; H 8.05

The preparation changed rapidly on standing, which explains the rather inaccurate analytical results.

The following were prepared by a similar method: β-formyl-β-methylvinyl ethyl ether with a b.p. of 91-93° at 19 mm; $n^{21}D$ 1.4740, λ_{max} (in alcohol) 252.5 mμ (ε 19100).

Found %: C 63.02; 63.21; H 8.70; 8.56
$C_6H_{10}O_2$. Calculated %: C 63.13; H 8.83

β-Formyl-β-amylvinyl ethyl ether with a b.p. of 126-129° at 13 mm; $n^{20}D$ 1.4729, λ_{max} (in alcohol) 253 mμ (ε 14750).

Found %: C 70.35; 70.42; H 10.60; 10.80
$C_{10}H_{18}O_2$. Calculated %: C 70.54; H 10.66

Hydrolysis of the tetraethylacetal of acetoacetaldehyde. The reaction was carried out in a manner similar to that described above. From 70.3 g of the tetraethylacetal was obtained 38.3 g of the diethylacetal of acetoacetaldehyde with a b.p. of 74.5° at 9 mm; $n^{19}D$ 1.4215.

Found %: C 59.84; 59.85; H 9.69; 9.70
$C_8H_{16}O_3$. Calculated %: C 59.98; H 10.07

The following were prepared in yields of 70-75%: the diethylacetal of propionylacetaldehyde with a b.p. of 93-96° at 17 mm; $n^{20}D$ 1.4238.

Found %: C 61.89; 62.05; H 10.13; 10.20
$C_9H_{18}O_3$. Calculated %: C 62.04 H 10.41

The diethylacetal of valerylacetaldehyde with a m.p. of 89-91° at 4 mm; $n^{22}D$ 1.4272.

Found %: C 65.64; 65.40; H 10.60; 10.61
$C_{11}H_{22}O_3$. Calculated %: C 65.31; H 10.96

Hydrolysis of the tetraethylacetal of β-ethoxygluteraldehyde. In a manner similar to that described above, 5.3 g of 2,4,6-triethoxytetrahydropyran with a b.p. of 112-115° at 10 mm, $n^{21}D$ 1.4340.

Found %: C 60.53; 60.54; H 10.29; 10.37
$C_{11}H_{22}O_4$. Calculated %: C 60.52; H 10.16

2,4,6-Triethoxy-3-methyltetrahydropyran was also prepared in 70% yield; b.p. 92-95° at 3 mm; $n^{23}D$ 1.4368.

Found %: C 62.18; 62.21; H 10.28; 10.32
$C_{12}H_{24}O_4$. Calculated %: C 62.04; H 10.41

Preparation of 5-(cyclohexen-1'-yl)-3-methylpentene-2-yne-4-al. To an ether solution of lithium cyclohexen-1-ylacetylide (prepared from 10.6 g of 1-ethynylcyclohexene and C_6H_5Li in ether) at 0° was added a solution of 16 g of the diethylacetal of acetoacetaldehyde in 25 ml of ether; the reaction mixture was stirred for an hour at 0° and an hour at room temperature, and was then refluxed for 4 hr. The mixture was treated with a saturated solution of ammonium chloride, and the ether layer was separated and dried with magnesium sulfate. Distillation separated 10.9 g of 5-(cyclohexen-1'-yl)-3-hydroxy-3-methyl-1,1-diethoxy-4-pentyne with a b.p. of 128-129° at 1 mm; $n^{22}D$ 1.4871.

Found %: C 72.42; 72.50; H 9.61; 9.87
$C_{16}H_{26}O_4$. Calculated %: C 72.14; H 9.84

A mixture of 8.4 g of this product, 35 ml of a solution of 11 g of sodium acetate in 7 ml of water, and 110 ml of acetic acid was heated on a boiling water bath under a slow stream of nitrogen. The mixture was poured onto ice and extracted with petroleum ether, and the extract was dried with magnesium sulfate. Distillation separated 3.1 g of 5-(cyclohexen-1'-yl)-3-methylpenten-2-yn-4-al with a b.p. of 128-130° (in the bath) at $6 \cdot 10^{-4}$ mm; $n^{18}D$ 1.5797.

The aldehyde was characterized by means of its 2,4-dinitrophenylhydrazone, m.p. 161-161.5°(from alcohol) and its semicarbazone, m.p. 199-200° with decomposition; these values correspond to those cited in the literature [5].

Preparation of diethyl 3-methyl-1,4-pentadiene-1,4-pentadiene-1,5-dicarboxylate. A mixture of 3.36 g of methylmalonaldehyde, 20.34 g of carboethoxymethylenetriphenylphosphorane, and 100 ml of benzene was refluxed under a slow stream of nitrogen for 4 hr. The benzene was distilled, and the residue was treated with petroleum ether, filtered, and distilled to obtain 1.95 g of diethyl 3-methyl-1,4-pentadiene-1,5-dicarboxylate with a b.p. of 151-154° at 4 mm; $n^{26.5}D$ 1.4950.

Found %: C 63.63; 63.67; H 7.99; 8.03
$C_{12}H_{18}O_4$. Calculated %: C 63.70; H 8.02

When 0.85 g of the ester was hydrogenated in methanol solution in the presence of platinum oxide, 172.1 ml of H_2 was absorbed (calculated for two double bonds, 165.7 ml H_2). Distillation yielded 0.62 g of diethyl 3-methylpentane-1,5-dicarboxylate with a b.p. of 93-94° at 3 mm, $n^{22.5}D$ 1.4402.

Found %: C 62.87; 62.71; H 9.65; 9.79
$C_{12}H_{22}O_4$. Calculated %: C 62.56; H 9.63

Preparation of 1,7-dicarboethoxy-4-ethoxy-3-methyl-1,6-heptadiene. The reaction was carried out in a manner similar to that described above. From 3 g of α-methyl-β-ethoxyglutaraldehyde was obtained 3.6 g of 1,7-dicarboethoxy-4-ethoxy-3-methyl-1,6-heptadiene with a b.p. of 166-168° at 2 mm; $n^{21.5}$ 1.4683.

Found %: C 64.11; 64.10; H 8.92; 8.96
$C_{10}H_{26}O_5$. Calculated %: C 64.40; H 8.78

Preparation of 1-carboethoxy-5-benzoyloxy-4-methyl-2,4-pentadiene. The reaction with β-formyl-β-methylvinyl benzoate was carried out in a manner similar to that described above. The resulting 1-carboethoxy-5-benzoyloxy-4-methyl-2,4-pentadiene had a m.p. of 119-121.5° (from a mixture of ether and petroleum ether).

Found %: C 69.02; 69.10; H 6.45; 6.50
$C_{15}H_{16}O_4$. Calculated %: C 69.21; H 6.20

Treatment of this compound with a hydrochloric acid solution of 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone with a m.p. of 159-161.5° (from methanol).

Found %: N 17.16
$C_{14}H_{16}O_6N_4$. Calculated %: N 17.66

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THERMODYNAMIC CHARACTERISTICS OF $BaMoO_4$ AND $BaMoO_3$ AND THE EQUILIBRIUM OF THESE COMPOUNDS WITH HYDROGEN

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The present work, which is a continuation of a series of investigations of the thermodynamics of tungstates and molybdates [1-4], was devoted to a study of the equilibrium between barium molybdate and hydrogen. The $BaMoO_4$ was prepared by precipitation from a solution of sodium molybdate with an equivalent amount of $Ba(NO_3)_2$ solution; the precipitate was carefully washed, dried, and calcined. The resulting $BaMoO_4$ had a tetragonal structure, the lattice constants of which were in good agreement with the literature values [5].

TABLE 1

Stage I		Stage II	
temp, °K	K_{P_I}	temp, °K	$K_{P_{II}}$
1479	0,084	1521	0,0348
1521	0,092	1562	0,0434
1562	0,102	1604	0,0550
1604	0,113	1645	0,0672
1687	0,126		

The equilibrium between $BaMoO_4$ and hydrogen over the temperature interval 1200-1400°C was studied by the circulation method using an apparatus described in reference [4]. X-ray investigation showed that reduction of $BaMoO_4$ in this temperature interval occurs with the formation of the intermediate compound $BaMoO_3$ (perovskite type, a = 4.03 A) [6]; the final reduction products are BaO and Mo. The BaO remains in the solid phase at these temperatures; according to references [7, 8], the vapor pressure of BaO at 1400°C does not exceed 0.001 mm Hg.

Thus, like the previously studied magnesium [9], calcium [1], and strontium molybdates, the reduction of $BaMoO_4$ by hydrogen takes place in two stages:

$$BaMoO_4 + H_2 \rightarrow BaMoO_3 + H_2O, \quad \text{(I)}$$

$$^1/_2 BaMoO_3 + H_2 \rightarrow {}^1/_2 BaO + {}^1/_2 Mo + H_2O. \quad \text{(II)}$$

Table 1 presents average values of the equilibrium constants $K_{pI} = P_{I\,H_2O}/P_{I\,H_2}$ and $K_{pII} = P_{II\,H_2O}/P_{II\,H_2}$ for Stages I and II of the reduction of $BaMoO_4$; values are given for a series of temperatures. Figure 1 is a graph showing the dependence of log K_{pI} and log K_{pII} on 1/T.

The relationship between the logarithm of the equilibrium constants for the two stages of reduction of $BaMoO_4$ and the reciprocal of the absolute temperature is described by the following equations (with an accuracy of ± 0.25% for the first stage and an accuracy of ± 0.2% for the second)

$$\lg K_{p_I} = -\frac{11155}{4,575T} + 0,5708, \quad \lg K_{p_{II}} = -\frac{26610}{4,575T} + 2,3639.$$

By combining Reactions (I) and (II), we obtain the equation for the complete reduction of $BaMoO_4$:

$$BaMoO_4 + 3H_2 \rightarrow BaO + Mo + 3H_2O. \quad \text{(III)}$$

For this reaction $\log K_{pIII} = \lg \frac{p^3_{III\,H_2O}}{p^3_{III\,H_2}} = \lg K_{pI} + 2 \lg K_{pII} = -\frac{64370}{4{,}575T} + 5{,}299$, $\Delta F^0_{III} = -RT \ln$

$K_{pIII} = 64370 - 24.24\,T$.

For the reduction of $BaMoO_3$ by hydrogen:

$$BaMoO_3 + 2H_2 \rightarrow BaO + Mo + 2H_2O, \qquad \text{(IIa)}$$

$$K_{pIIa} = K^2_{pII}; \quad \Delta F^0_{IIa}\,(\text{cal}) = -4{,}575\,T \lg K^2_{pII} = 5321\,Q - 21{,}63\,T.$$

Values of ΔF^0_{IIa} and ΔF^0_{III}, and also of ΔH_{IIa} and ΔH_{III} are shown in Table 2 for a series of temperatures. By combining reactions IIa and III with the reaction for the formation of water vapor

$$H_2 + \tfrac{1}{2}\,O_2 \rightleftarrows H_2O\,(g), \qquad \text{(IV)}$$

the Gibbs free energy change and heat content change of which are given by the following equations (according to Chipman [10])

$$\Delta F^0_{IV}\,(\text{cal}) = -59251 + 2{,}006\,T \lg T - 7{,}5 \cdot 10^{-5} T^2 + \frac{408\,000}{T} + 6{,}8085\,T,$$

$$\Delta H_{IV}\,(\text{cal}) = -59251 - 0{,}871\,T + 7{,}5 \cdot 10^{-5} T^2,$$

it is possible to calculate* ΔF^0_V (and, correspondingly, ΔH_V) and ΔF^0_{VI} (and, correspondingly, ΔH_{VI}) for the formation of $BaMoO_3$ and $BaMoO_4$ in accordance with the reactions:

$$BaO + Mo + O_2 \rightarrow BaMoO_3 \qquad \text{(V)}$$

$$BaO + Mo + {}^3/_2 O_2 \rightarrow BaMoO_4. \qquad \text{(VI)}$$

The calculated values of ΔF^0_V and ΔF^0_{VI} are shown in Table 2. The temperature dependence of these quantities over the temperature range investigated is expressed by the equations:

$$\Delta F^0_V\,(\text{cal}) = -\Delta F^0_{IIa} + 2\Delta F^0_{IV} = -173\,020 + 49{,}19\,T,$$

$$\Delta F^0_{VI}\,(\text{cal}) = -\Delta F^0_{III} + 3\Delta F^0_{IV} = -244\,070 + 65{,}58\,T.$$

It was not possible to calculate ΔF^0_V at 298°K owing to the lack of data on the heat capacity of $BaMoO_3$. For

TABLE 2

T, °K	ΔF°_{IIa}, kcal	ΔH_{IIa}, kcal	ΔF°_{III}, kcal	ΔH_{III}, kcal	ΔF°_{IV}, kcal	ΔH_{IV}, kcal	ΔF°_V, kcal	ΔH_V, kcal	ΔF°_{VI}, kcal	ΔH_{VI}, kcal
1473	21,36		28,67		−39,75		−100,56		−147,47	
1523	20,27		27,45		−39,07		−98,10		−144,20	
1573	19,19	53,22	26,17	64,37	−38,38	−59,90	−95,64	−173,0	−140,87	−244,07
1643	17,68		24,54		−37,42		−92,20		−136,32	

BaO, Mo, and O_2 [11] and $BaMoO_4$ [12] there are available the following equations relating the true molar heat capacities to temperature:

Mo: $c_p = 5{,}48 + 1{,}30 \cdot 10^{-3} T$;
O_2: $c_p = 8{,}27 + 0{,}258 \cdot 10^{-3} T - 1{,}877 \cdot 10^5 T^{-2}$;
BaO: $c_p = 12{,}74 + 1{,}04 \cdot 10^{-3} T - 1{,}984 \cdot 10^5 T^{-2}$;
$BaMoO_4$: $c_p = 25{,}37 + 13{,}38 \cdot 10^{-3} T$.

*In this calculation, we used the simpler equation $\Delta F^0_{IV} = -59{,}000 + 13.782\,T$, which may be obtained from the Chipman equation for the temperature interval 1473-1643°K.

Using these equations and our data, we obtain the following equation for the temperature dependence of ΔF^0_{VI} over the temperature interval from 299 to 1643°K:

$$\Delta F^0_{VI} = -248520 + 5{,}255\,T \ln T - 5{,}325 \cdot 10^{-3} T^2 - \frac{2{,}4 \cdot 10^5}{T} + 38{,}21\,T,$$

whence, at 298.2°K: ΔF^0_{VI} = - 229.5 kcal/mole; ΔH^0_{VI} = - 251.2 kcal/mole; and ΔS^0_{VI} = - 72.9 e.u. Taking the standard molar entropies of BaO, Mo, and O_2 as, respectively, 16.8, 6.83, and 49.00 e.u. [13], we obtain $(BaMoO_4)S_{298.2}$ = 24.2 e.u.

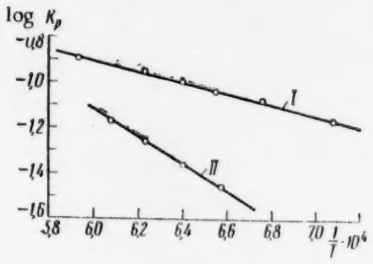

Fig. 1.

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• See C. B. translation.

ON THE MECHANISM OF THE REACTION BETWEEN PALLADIUM SALTS AND OLEFINS IN HYDROXYL-CONTAINING SOLVENTS

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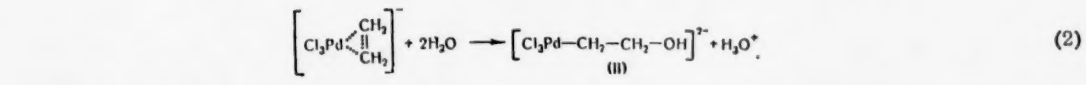
The formation of carbonyl compounds during the reaction of olefins with palladium salts in aqueous solution proceeds through a stage in which a π-complex of the type $[Cl_3PdC_nH_{2n}]^-$ interacts with water according to the equation:

$$[Cl_3PdC_nH_{2n}]^- + H_2O = Pd + 2HCl + Cl^- + C_nH_{2n}O. \quad (1)\bullet$$

In considering the mechanism of this reaction, we have proposed [1] that during the course of the decomposition of the π-complex, cleavage of a proton from the doubly bonded carbon atom takes place, and the π-complex is converted to a metalloorganic compound (a compound of the type $CH_2 = CH-PdCl_3^{2-}$, I, in the case of ethylene). A vinyl alcohol is formed by the reaction of I with water, and this then isomerizes to the carbonyl compound.

Other authors [2] consider that the first stage of Reaction (1) is the addition of an HO^- ion to the highly polarized olefin. Without entering into a detailed discussion of this question before more detailed data are obtained, we may mention that participation of HO^- ions in this reaction seems improbable to us. In particular, the absolute concentration of HO^- ions was 10^{-12}-10^{-14} gram ions/liter in our experiments, and the concentration of such nucleophilic ions as Br^- and Cl^- exceeded the concentration of HO^- ions by a factor of 10^{10}-10^{12}. It is evident that under these conditions reaction of the π-complex with halogen ions (leading ultimately to the formation of organic halogen compounds, which are reasonably stable under the conditions of the experiment) must take place, to some extent at least, concurrently with the reaction of the π-complex with HO^- ions. Thus, such a scheme cannot satisfactorily explain the high selectivity of the oxidation process—a selectivity high enough that the yield of carbonyl compounds reaches 95-99%.

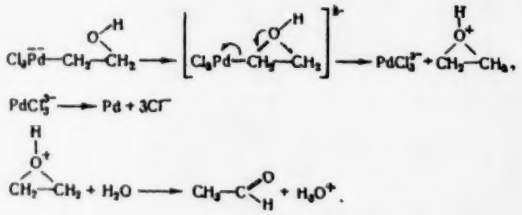
A more acceptable mechanism would seem to be one in which the charge on the nucleophilic particle attacking the carbon atom at the olefinic double bond in the π-complex has no essential significance, and the addition of the HO^- ion takes place as a result of the reaction of the π-complex with a solvent molecule:



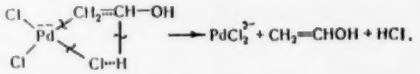
(II) (2)

•It is also possible that, in actual fact, it is not the complex anion which directly undergoes decomposition, but a complex of the type $Cl_2PdC_nH_{2n}$ or $[ClPdC_nH_{2n}]^+$. In this case, the equation for the reaction and the forms of the activated complexes (see below) would change correspondingly.

If one may judge, for example, by analogy to organomercury compounds, the resulting β-chloropalladium-substituted ethanol (II) should readily undergo acidolysis to the alcohol. The absence of alcohol among the reaction products may possibly be explained on the basis that the conversion of II to the carbonyl compound takes place more rapidly than acidolysis. This reaction can proceed by two routes: 1) through the α-oxide; 2) through the vinyl alcohol. In the first case, the reaction proceeds via an intramolecular nucleophilic substitution, type SN_i:



Formation of vinyl alcohol could take place through the conversion of II through a five-membered active complex:



Essential information on the mechanism of the decomposition of the π-complex may be obtained through a study of the reaction between $PdCl_2$ and olefins in nonaqueous solvents. It is evident that this should permit isolation of the corresponding derivatives of the intermediate compounds formed when the reaction is carried out in water. Thus, if the reaction proceeds through the α-oxide, the formation of glycol ethers or esters would be expected when the reaction is carried out in solution in alcohol or a carboxylic acid, respectively. On the other hand, if the reaction proceeds through vinyl compounds, the formation of vinyl ethers or esters or their conversion products would be expected. Smidt and co-workers [2] reported that palladous chloride is not reduced by the action of olefins in glacial acetic acid. These solutions absorb olefins, and the excess olefin over that dissolved in the absence of $PdCl_2$ is equivalent to the amount of $PdCl_2$ dissolved. This fact can be considered as evidence of the reversible formation of a π-complex between $PdCl_2$ and the olefin in these solutions.

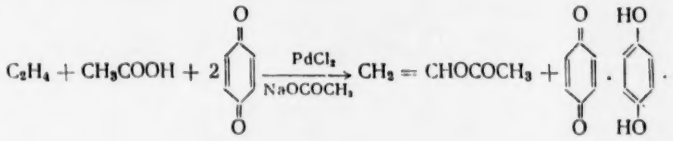
The absence of reduction in glacial acetic acid may be ascribed to various causes. One such possible cause is that the interaction between $PdCl_2$ and olefins under these conditions is completed through the formation of a complex which is different in structure from that formed during the reaction of $PdCl_2$ with olefins in water. In an effort to confirm this assumption, we attempted to carry out a reaction between glacial acetic acid and the complex $(PdCl_2 \cdot C_2H_4)_2$, which we synthesized by the method of Kharasch [3]. Our experiments showed that this compound, which reacts instantaneously even with atmospheric moisture, remains unchanged over a period of ten days in glacial acetic acid. Moreover, the $(PdCl_2 \cdot C_2H_4)_2$ complex decomposes with the liberation of metallic palladium in ethyl alcohol, benzyl alcohol, and phenol solutions.

It is possible that the basic reason for the hindrance of the decomposition of the π-complex in glacial acetic acid is the "acid character" and the decreased nucleophilic nature of the solvent molecules, which tend more toward the removal of a proton than the formation of onium ions. As a result, the first stage in the decomposition of the π-complex is hindered. If this is the case, then the addition of lyate ions (for example, in the form of an alkali metal) to the solution should make possible reaction of the π-complex with the acid. Our experiments showed that palladous chloride in acetic acid solution containing sodium acetate reduces ethylene according to the equation:

$$C_2H_4 + PdCl_2 + 2CH_3COONa \rightarrow CH_2 = CH - OCOCH_3 + 2NaCl + Pd + CH_3COOH. \quad (3)$$

The yield of vinyl acetate was 97%, based on the ethylene reacted. The $(PdCl_2 \cdot C_2H_4)_2$ complex also reacts with sodium acetate in glacial acetic acid with the formation of vinyl acetate. In the presence of substances which can oxidize the metallic palladium formed during the reduction, Reaction (3) can obviously be used for the preparation of vinyl esters. Thus, for example, in the presence of p-benzoquinone, oxidation of the

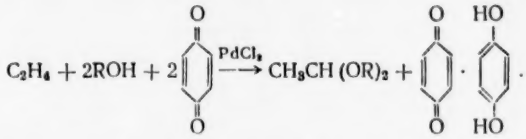
palladium proceeds simultaneously with Reaction (3). The over-all reaction can be represented by the equation:



If it is assumed that decomposition of the π-complex in alcohol proceeds analogously to decomposition in acetic acid, it would be expected that the product of the reaction of $PdCl_2$ with ethylene in solution in alcohol would be a vinyl ether or the product of the addition of a molecule of alcohol to it (a reaction which is catalyzed by traces of acid or metal halides [4]). Our experiments showed that $(PdCl_2 \cdot C_2H_4)_2$ reacts rapidly with alcohol. The chief product of the reaction is acetal:

$$(PdCl_2 \cdot C_2H_4)_2 + 4C_2H_5OH \rightarrow 2Pd + 4HCl + 2CH_3CH(OC_2H_5)_2. \quad (4)$$

In the presence of p-benzoquinone, reduction of $PdCl_2$ with ethylene in alcohol solution is accompanied by oxidation of the metallic palladium, which allows this reaction to be used for the preparation of acetals directly from olefins:



Copper salts can also be used as the oxidizing agent in alcoholic solutions; this is similar to the use of these salts when the reaction is carried out in aqueous solution [1, 2].

Out data are substantial confirmation of the point of view that decomposition of the π-complex in hydroxyl-containing solvents proceeds through the intermediate formation of vinyl compounds. In water, this vinyl compound is vinyl alcohol, which isomerizes to acetaldehyde; in acetic acid, it is vinyl acetate, and in alcohol, it is a vinyl ether, which then adds a molecule of alcohol with the formation of acetal. Obviously, the data obtained in the present work are difficult to explain if it is considered that the reaction proceeds through the α-oxide.

It should be remarked that our data do not answer the question of which of the two reactions—conversion of the π-complex to I or II—is the first act of decomposition. In particular, both mechanisms explain both the absence of reaction in glacial acetic acid and the fact that in the presence of CH_3COO^- ions, reaction of the π-complex with acetic acid becomes possible. However, the weak spot in the mechanism which includes Reaction (2) as the first stage is the assumption that the conversion of the vinyl compound proceeds more rapidly than does acidolysis of II.

EXPERIMENTAL

1. Interaction of $(PdCl_2 \cdot C_2H_4)_2$ complex with nonaqueous solvents. a) The $(PdCl_2 \cdot C_2H_4)_2$ complex, 2.05 g (0.005 mole), prepared from the compound of palladium with benzonitrile by the method of Kharasch [3], was mixed with 1.58 g (0.034 mole) of absolute alcohol. Heat was evolved, and metallic palladium rapidly precipitated. After two hours, the solution was filtered and distilled. A fraction boiling at 102-104°/758 mm was collected; the yield was 0.74 g; d^{20}_4 0.8252, $n^{20}D$ 1.3818. b) The same amount of the $(PdCl_2 \cdot C_2H_4)_2$ complex, 2.05 g (0.005 mole), was mixed with 1.5 ml (0.025 mole) of glacial acetic acid. No changes were observed over a period of ten days. c) Similarly, 2.05 g (0.005 mole) of the $(PdCl_2 \cdot C_2H_4)_2$ complex was mixed with 1.5 ml (0.025 mole) of glacial acetic acid and 0.41 g (0.005 mole) of anhydrous sodium acetate. Metallic palladium precipitated rapidly. After three hours, the solution was filtered, washed with water, dried with magnesium sulfate, and distilled. A fraction boiling at 72-73° was collected; the yield was 0.51 g; d^{20}_4 0.9341, $n^{20}D$ 1.3958.

	Found %:	C 55.50; 55.66; H 7.38; 7.26
$C_4H_6O_2$.	Calculated %:	C 55.80 H 7.03

The infrared spectrum was identical with that of vinyl acetate (bands at 1775, 1660, 1438, 1377, 1298, 1226, 1146, 1025, 980, 955, 880 and 851 cm^{-1}).

2. Interaction of palladous chloride with ethylene in solution in glacial acetic acid containing sodium acetate. A solution of 8.88 g (0.05 mole) of anhydrous palladous chloride and 8.2 g (0.10 mole) of anhydrous sodium acetate in 60 ml of glacial acetic acid at 20° was saturated with dry ethylene over a period of 16 hr. After the absorption of 560 ml (at 765 mm) of ethylene (0.0235 mole) the precipitated palladium was filtered off, and a fraction boiling at 96-118° was distilled (24 ml). The unsaturates content, as determined by means of Kaufmann reagent, was 0.0228 mole (97% of the absorbed ethylene). This fraction was distilled in a column (33 theoretical plates), and a fraction boiling at 72-86° was collected. This fraction was washed with water, dried with magnesium sulfate, and distilled. The yield was 0.84 g of a fraction boiling at 72.4-72.9°/755 mm; d^{20}_4 0.9340, $n^{20}D$ 1.3958. The i.r. spectrum was identical to that of vinyl acetate (see 1c).

3. Oxidation of ethylene with p-benzoquinone in acetic acid in the presence of palladous chloride. A solution of 0.178 g (0.001 mole) of anhydrous palladous chloride and 8.2 g (0.1 mole) of anhydrous sodium acetate in 125 ml of glacial acetic acid was mixed with 27 g (0.25 mole) of p-benzoquinone, and the mixture was stirred and saturated with dry ethylene over a period of 63 hr at 18°. After the absorption of 2100 ml (at 765 mm) of ethylene (0.0885 mole), the solution was filtered, and a fraction boiling at 85-118° (60 ml) was distilled from the filtrate. After a second distillation with a dephlegmator the unsaturates content, as determined by means of Kaufmann reagent, was 0.0877 mole (99.2% of the ethylene absorbed). This mixture was distilled in a column (33 theoretical plates), and the fraction boiling at 72-86° was washed with water, dried with magnesium sulfate, and distilled. The yield was 3.27 g of a fraction boiling at 72.5-72.9°/758 mm; d^{20}_4 0.9341, $n^{20}D$ 1.3959; the i.r. spectrum was identical to that of vinyl acetate.

4. Oxidation of ethylene with p-benzoquinone in alcoholic solution in the presence of palladous chloride. To a solution of 0.500 g (0.00281 mole) of anhydrous $PdCl_2$ in 29 ml (23 g or 0.5 mole) of absolute alcohol was added 25 ml of absolute ether and 54 g (0.5 mole) of p-benzoquinone. The mixture was stirred and saturated with dry ethylene over a period of 6 hr at 18°. After the absorption of 5500 ml (at 765 mm) of ethylene (0.233 mole) 50 ml of ether was added; the solution was filtered and the filtrate was washed with 10% aqueous KOH until no further decolorization occurred, dried with magnesium sulfate, and distilled. The yield was 19.9 g (72.4% based on the ethylene reacted) of a fraction boiling at 102-104°; d^{20}_4 0.8252, $n^{20}D$ 1.3816.

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• Original Russian pagination. See C. B. translation.

ISOMERIZATION OF THE n-PROPYL FREE RADICAL IN SOLUTION

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In 1941, Kharasch and co-workers [1] decomposed n-butyryl peroxide and isobutyryl peroxide in carbon tetrachloride, and they found that only n-propyl chloride was formed in the first case, while isopropyl chloride was exclusively formed in the second case. On the basis of these results, Kharasch concluded that alkyl free radicals are incapable of isomerization.

By using the C^{14} isotope of carbon, we have found that the propyl free radical formed during thermal decomposition of n-butyryl peroxide in solution in accordance with the reaction:

$$(CH_3CH_2CH_2COO)_2 \rightarrow 2CH_3 - CH_2 - CH_2\bullet + 2CO_2,$$

undergoes isomerization of the following type:

$$CH_3 - CH_2 - C^{14}H_2\bullet \rightleftarrows \cdot CH_2 - CH_2 - C^{14}H_3.$$

Decomposition of the n-butyryl peroxide labeled in the alpha position was carried out in boiling carbon tetrachloride:

$$(CH_3 - CH_2 - C^{14}H_2 - COO)_2 + 2CCl_4 \rightarrow 2CH_3 - CH_2 - CH_2 - Cl + 2CO_2 + CCl_3 - CCl_3.$$

In order to establish the position of the C^{14} atom in the propyl chloride molecule, the latter was hydrolyzed to n-propyl alcohol, the alcohol was oxidized to propionic acid, and the propionic acid was oxidized to acetic acid:•

$$CH_3 - CH_2 - CH_2 - Cl \xrightarrow[(K_2CO_3)]{H_2O} CH_3 - CH_2 - CH_2 - OH \xrightarrow{KMnO_4}$$

$$\rightarrow CH_3 - CH_2 - \overset{\displaystyle O}{\overset{\|}{C}}\!\!-\!\!OH \xrightarrow{K_2Cr_2O_7} CH_3 - \overset{\displaystyle O}{\overset{\|}{C}}\!\!-\!\!OH$$

The acetic acid was active (about 4% of the activity of the original peroxide). It follows from this fact that some of the n-propyl radicals had undergone rearrangement.

In establishing the position of the C^{14} carbon in the acetic acid molecule, two routes were used: alkaline fusion of its sodium salt, on the one hand, and Schmidt cleavage, on the other:

a) $CH_3 - COONa + NaOH \rightarrow C^{14}H_4 + Na_2CO_3$,
b) $CH_3 - COOH + HN_3 \rightarrow C^{14}H_3 - NH_2 + CO_2 + N_2$.

•Special experiments established that rearrangement of the propyl chloride did not occur during the hydrolysis.

In the first case, we established that the sodium carbonate formed was inactive. In the second case, it was found that all of the activity of the acetic acid had been transferred to the methylamine.

From the acetic acid and methylamine activities obtained in three parallel experiments, it follows that isomerization of the n-propyl radical under the indicated conditions amounted to 4.0 ± 0.5%.

Thus, the n-propyl radical isomerizes in solution with migration of a hydrogen atom from the beta position,* and not with migration of the methyl group, $CH_3-CH_2-C^{14}H_2 \cdot \rightleftharpoons \cdot CH_2-C^{14}H_2-CH_3$, as we had at first considered [3] on the basis of an analogy with the results obtained by Roberts and Halmann [4] in a study of the isomerization of the propylium cation.

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*V. V. Voevodskii and R. E. Mardaleishvili [2], in a study of the exchange of free radicals with deuterium, were the first to show that it is possible for free radicals to isomerize in the vapor phase by migration of hydrogen at atoms from the beta position. That alkyl radicals do not isomerize in solution by migration of hydrogen atoms from the alpha position follows from the work of Kharasch cited above [1].

**Original Russian pagination. See C. B. translation.

ON THE HYDROLYTIC DECOMPOSITION OF OXIDIZED COALS

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(Presented by Academician M. M. Shemyakin, January 12, 1960)
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Original article submitted January 10, 1960

In studies of the chemistry of coal, considerable attention has been given to humic acids, the formation of which from coal is closely connected with hydrolysis of the organic portion of coal in alkaline media [1]. The introduction of polar functional groups into the coal macromolecule considerably facilitates the occurrence of hydrolysis reactions [2]. However, the resulting low molecular weight compounds have a considerable number of double bonds and polar groups, which makes their investigation more difficult. Considering these data and the theoretical scheme of hydrolytic decomposition due to M. M. Shemyakin [3], it was decided to use the Kolbe carboxylation reaction, which proceeds smoothly with higher phenols.

The characteristics of the oxidized coal from the Kaa-Khem formation of the Tuva ASSR are shown below. This was first concentrated by the method of I. I. Ammosov [4] and then by a chemical method (10% HCl and 4% H_2F_2):

Chemical Composition of the Coal (in percent)

Petrographic comp., %	A**	S_{tot}	C	H	N	O by diff.	COOH groups*	Phenolic OH groups*	Yield of humic acids
99.9 clarain	0.12	0.30	67.22	3.88	1.59	27.01	1.97	3.69	43-45

*Determined by a chemisorption method; values are in milliequivalents per gram.
**Ash, dry basis—Publisher's note.

As may be seen from these data, the coal can be considered as a peculiar polyphenol which can be carboxylated by the Kolbe reaction [5]:

$$ROH \xrightarrow{NaOH;\ CO_2} R(OH)COONa \qquad (I)$$

with subsequent hydrolysis of the olefinic double bonds [3]:

$$>C=C< + H_2O \rightarrow >CH-C(OH)< \rightarrow >CH_2 + O=C<. \qquad (II)$$

The simultaneous occurrence of the two reactions should reveal the previously unknown specific structure of the organic matter of the coal.

Characteristics of the Low Molecular Weight Hydrolysis Products

Fraction	Product	C	H	N	S	Br	OCH_3	O, by diff.	C/H, atom	H/O, atom	Acid No.	Sap. No.	Mol. wt.
Acid	Acids	55,78	4,13	1,44	0,76	—	1,51	39,33	1,13	1,69	76,9	102,5	—
	Acid reduction products	68,80	5,85	1,58	1,36	—	—	28,39	0,98	3,22	—	—	
	Acid bromination products	48,84	3,35	—	—	22,45	—	~25,36	1,27	~1,84	—	—	120,5 ($in H_2O$)
	Acid oxidation products	44,25	3,85	—	—	—	—	~51,40	~1	~1	320,5	270,5	
Neutral	Neutral	74,37	8,42	0,75	—	—	—	16,46	0,73	7,81	—	273	163,2 (dioxane)
	Bromination products	44,82	5,60	—	—	37,53	—	~12,05	0,67	~7,4	—	—	—
	2,4-Dinitrophenylhydrazones	39,51	3,7	27,36	—	—	—	29,42	—	—	—	—	—
Basic	Coal bromination products	40,07	2,65	—	—	42,81	—	~14,47	1,27	~2,76	—	—	—
	Coal oxidation products	45,16	4,84	3,32	—	—	—	46,68	0,8	1,83	373,8	306,4	94,5 ($in H_2O$)

To 40 g of coal was added 400 ml of a 15% aqueous solution of NaOH; the mixture was made homogeneous by stirring, and a stream of CO_2 was then passed through the mixture at a rate of 1.2-1.3 liters/hour. The experiment was continued for 24 hr at 94-98°C, after which the mixture was acidified to a pH of 3. The solid matter was filtered off, washed, and extracted with hot 70% alcohol, which removed 22.1% of a brown, tarry acid product. The coal remaining on the filter was almost completely soluble in alkalies; i.e., it was humic acids. It was found that 94.7% of the organic matter of the coal could be transferred to the alcoholic solution by repeating these operations eight times. As M. M. Shemyakin and I. A. Red'kin have shown [6], under the conditions described here the formation of a certain amount of acids and alcohols would be expected, in addition to the formation of ketones by Scheme II. We investigated the low molecular weight, alcohol-soluble products obtained in the first stage of the hydrolysis of the coal. Acetic acid (0.75% yield based on the organic material of the coal or 3.28% based on the total amount of low molecular weight products) and formic acid (less than 0.001%) were found in the transparent, colorless liquid obtained after acidification of the reaction mixture. By successive treatments with 10% HCl and 10% NaOH, the alcohol-soluble product was separated into there parts: acidic, basic, and neutral (yields were 88.9%, 0.091%, and 10.92%, respectively). The table presents the analytical characteristics of these products.

In alkaline solution the acids reacted with benzoyl chloride, giving amorphous acid esters (16.4% weight increase). With thionyl chloride the acids formed amorphous acid chlorides, from which amides, anilides, and esters could be prepared. In alcoholic solution the acids reacted with semicarbazide (11.3% weight increase). Replacement of the oxygen in the rings by nitrogen was carried out in 25% NH_4OH saturated with NH_4Cl; the reaction was carried out in ampoules at 155-160° over a period of 12 hr. The resulting product was similar to that previously described [2], but it differed in that with $FeCl_3$ in dilute hydrochloric acid it gave an intense dark raspberry color characteristic of pyrrole rings. The x-ray pattern of the acids had only a single broad band. The infrared absorption spectra showed the presence of $>CO$, $-COOH$, $>CH_2$ and $-CH_3$ and the absence of unconjugated bonds. The bromine derivatives were prepared by the action of bromine water on the corresponding products, and the reduction products were prepared by reduction of the alcoholic solutions with Zn + HCl. Oxidation was accomplished by the method of Dilthey [7] by carefully adding perhydrol to the acetic acid solution. The yield of light yellow, amorphous oxidation products was not less than 80%. A color change characteristic of quinones of the chroman series was noted, and during the determination of the saponification numbers of the oxidation products it was found that the saponification number decreased with time. Both of these facts are similar to the observations made by

John [8] and Hooker [9] in the chroman series, and, in our opinion, they are connected with opening and closing of rings. The molecular weights of the products were determined cryoscopically (see the table); both dioxane and water were used as solvents. The sodium salts were used in the determination of the average molecular weights of the acid mixtures; consequently, it can only be said that the molecular weight of the acids was not lower than 420 and not higher than 800. Thus, our experimental data clearly show that hydrolytic decomposition occurs during carboxylation of coal. Consequently, we have observed here the dual specific reactivity of coal, which, on the one hand, behaves as an aromatic compound, and, on the other, as an olefin. As Fuchs has shown [10], a similar phenomenon is observed during bromination of coal [1]. In our opinion this feature of the reactivity is connected with, on the one hand, the noncoplanar structure, which is unequivocally shown by x-ray structural analysis, and, on the other hand, by the homoannular character of the addition reaction. The composition and properties of the hydrolysis and oxidation products of coal indicate that a specific system of conjugated double bonds, and not a hexagonal aromatic structure as proposed by van Krevelen [11], is basic in the structure of coal. We turn now to a consideration of the ease with which the carboxylation reaction occurs. The data suggest that under specific conditions in nature, humic acids can be formed in the soil without the participation of plants and animals; i.e., this is probably another important cycle by which the carbon cycle is completed in nature, but which has not been considered in geochemistry [12]. In conformity with theoretical concepts of hydrolysis [3], reconsideration of the position of the role of water in coal metamorphosis [13] is necessary. Indeed, without the concept of hydrolysis, it is impossible to understand why there are no coals in nature which do not contain water.

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ON THE NATURE OF THE CHEMICAL BOND IN MOLECULES OF ACETYLACETONATES OF TRIVALENT METALS

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The present work was devoted to an x-ray investigation of crystals of aluminum (I), chromium (II), and cobalt (III) acetylacetonates, which are isomorphic crystals. The unit cell dimensions and information on polymorphism and isomorphism in this series of compounds have been reported in our earlier communications [1-3]. The crystals of acetylacetonates were separated from solutions of these compounds in benzene, acetone, or chloroform by slow evaporation of the solvent. The exposures were carried out with copper radiation. Owing to a certain amount of disorder, crystals of II and III gave a limited number of reflections (642 and 316, respectively). The crystals of I gave 1373 reflections. The three-dimensional patterns of I and II consisted of data obtained by x-ray goniometric resolution of 0-5 layer lines along the b axis of the crystal; 0-4 layer lines were used for III. The blank spaces in the data were filled in by data obtained by resolution of layer lines along the other axes. In the first stage of the work, conversion of the structural factors to unit scale was carried out by comparing data from individual reflections along different axes, reflections common to all x-ray patterns being selected for this purpose; in subsequent stages, the conversion was made by comparing the experimental and theoretical values of the structural amplitudes for a series of $\sin\vartheta/\lambda$ intervals [4]. The structural investigation was carried out by the method of differential projection and planar and linear sections of the three-dimensional electron density. The isomorphic substitution method was used in the work.

Values for average interatomic distances and valence angles in the molecules of I, II, and III are presented below:

	I	II	III		I	II	III
Me—O	1,95±0,02Å	1,90±0,03Å	1,92±0,03Å	O—Me—O	89°±1°	93°±1°	90°±1°
C—C	1,38±0,04	1,40±0,04	1,41±0,04	Me—O—C	131 ±2	131 ±3	132 ±3
C—O	1,28±0,02	1,28±0,04	1,27±0,04	C—C—C	128 ±3	127 ±4	130 ±4
C—CH_3	1,53±0,03	1,53±0,04	1,52±0,04	O—C—C	122 ±4	118 ±4	118 ±4

In these acetylacetonates, the metal atom forms six equivalent covalent bonds, and the C = C and C = O double bonds in the acetylacetonate ring are delocalized. On the basis of the data presented above, it may be be assumed that the nature of the Me—O bond and the delocalization of the double bonds in the acetylacetonate ring do not depend on the electronic states in the d orbitals of the metal atoms.

In molecules of the acetylacetonates of the transition metals, both those having paired electrons and those not having paired electrons, and in the molecule of aluminum acetonate, in which the metal has no d electrons, delocalization of the double bonds is independent of the nature of the metal atom. This conclusion is in agreement with the data of D. N. Shigorin [5], who showed that the i.r. spectra of various acetylacetonates, including I, II, and III, are analogous. On the basis of the values obtained for the interatomic distances, it can be assumed that the formation of multiple Me—O bonds involving unshared pairs of d electrons of the metal atoms and the

$p\pi$ -electron of the oxygen atoms, as proposed by a number of authors [6, 7], does not occur. The π - Me−O bonds, upon delocalization of the double bonds, supplement the conjugated system of C = O and C = C bonds as a third multiple bond so that a "benzenoid" structure arises in the acetylacetonate ring [8], but these bonds are apparently of a different nature, which has no connection with the d electrons of the metal atom. It is possible that the p orbitals of the metal atoms are used in this over-all system of π interaction in the acetylacetonate ring [9].

The proposal that d electrons of the metal atom do not participate in the Me−O multiple bonds is in agreement with the concepts of crystal field theory. According to available experimental data, the acetylacetonate group, $C_5H_7O_2^-$, does not have a strong crystal field [8], and, consequently, it cannot cause forced coupling of d electrons, it cannot change their energy state to any great extent, and it cannot interact with them. This is confirmed by data on the magnetic moments: Nickel and iron cyanides are diamagnetic or, in any case, have a decreased spin; nickel and iron acetylacetonates are paramagnetic, and the magnetic moment of iron acetyl acetonate corresponds to five unpaired electrons.

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ON THE EXISTENCE OF CIS- AND TRANS-DIAQUOBISDIMETHYLGLYOXIMOCOBALT(III) SALTS

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Complex compounds of trivalent cobalt with dimethylglyoxime of the type $[CO\ A_2(DH)_2]X$ (a), $[Co\ A(DH)_2X]$ (b), and $H[Co(CH)_2(NO_2)_2]$ (c) were discovered by L. A. Chugaev [1-3].

On the basis of the trans-effect rules of I. I. Chernyaev, in 1954 one of us presented evidence that in the latter compound the two nitro groups are located trans to each other, and, consequently, the two dioximide groups lie in the same plane [4]. Further study confirmed this spatial configuration for diacidobisdimethylglyoximato cobalt(III) ions [5-7]. In the work reported in reference [4] it was shown that cobalt dioximines—the dinitro acid, the nitroaquo compound, and the chloronitro acid—retain their steric configuration during chemical conversions. In 1955, Nakahara [8, 9] showed by an independent route based on a study of the infrared spectra that the dioxime groups in $H[Co(DH)_2Cl_2]$, $H[Co(DH)_2(NO_2)_2]$, and certain other cobalt dioximines of the type of (a), (b), and (c) are located in the same plane.

A spectrophotometric study of the removal of a proton from cobalt dioximes has shown graphically that dioximines of all three types (a, b, and c) behave similarly. In all of the cases studied, there was an increase in the intensity and a shift of the bands at 245-250 mμ to the 250-260 mμ region and of the bands at 300 mμ to the 280 mμ region.

In 1957, A. V. Ablov and N. M. Samus' [10] prepared the hydroxoaquo compound $[CoH_2O \cdot (DH)_2OH] \cdot H_2O$ by the action of a concentrated solution of potassium carbonate on chlorobisdimethylglyoximocobalt (III) in the cold. When this chloroaquo compound, and also other acidoaquo compounds, was heated with concentrated (50%) potassium hydroxide solution, potassium dihydroxobisdimethylglyoximocobalt (III), $K[Co(DH)_2(OH)_2] \cdot 3H_2O$, was isolated. The action of HNO_3 on the latter compound gave diaquobisdimethylglyoximocobalt (III) nitrate $[Co(H_2O)_2(DH)_2]NO_3$.

During a spectrophotometric study of these compounds, we observed that, contrary to expectations, the light absorption curves of hydroxobisdimethylglyoximoaquocobalt and potassium dihydroxobisdimethylglyoximocobalt (III) in a medium sufficiently acid to guarantee that the compounds were completely converted to the diaquo compounds were not in agreement (Fig. 1). Two different absorption curves were also obtained when the spectra of these compounds were taken in sufficiently alkaline medium to guarantee that only the dihydroxo anions were present in both cases.

The spectra were taken with an SF-4 indicating quartz spectrophotometer at 15-17°. The concentration of the aqueous solutions used was 10^{-3}M in all cases. Curves for which no time is indicated for the action of acid or base were obtained immediately after the compound was dissolved. The exposure time did not exceed 20-25 min.

The assumption that the dihydroxo salt prepared under harsh conditions [10] is contaminated with decomposition products must be discarded, since spectra of this compound prepared by different synthesis routes agreed.

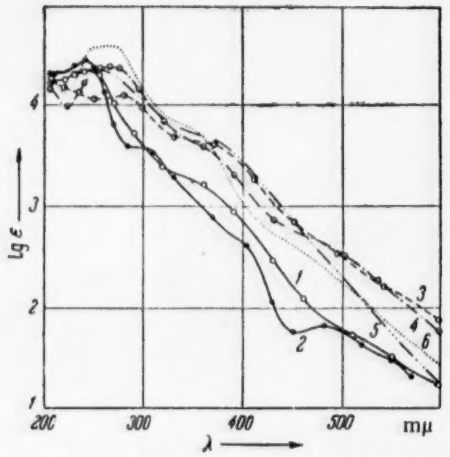

Fig. 1. Light absorption curves. 1) $[CoH_2O(DH)_2 \cdot OH] \cdot H_2O$; 2) $[CoH_2O(DH)_2OH] \cdot H_2O$; 3) $K[Co(DH)_2(OH)_2] \cdot 3H_2O$; 4) $K[Co(DH)_2(OH)_2] \cdot 3H_2O$; 5) $[Co(DH)_3] \cdot 3H_2O$ in 0.01 N $HClO_4$; 6) $[Co(DH)_3] \cdot 3H_2O$ in 0.01 N KOH.

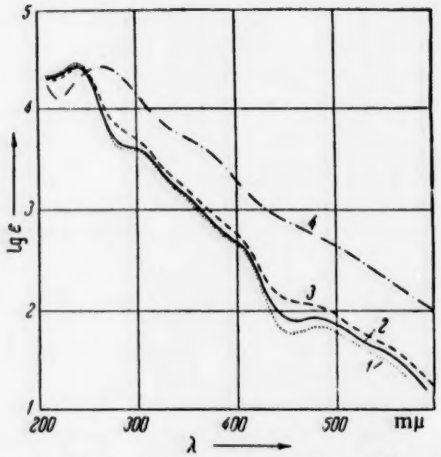

Fig. 2. Absorption curves for hydroxobisdimethylglyoximoaquocobalt. 1) In $2 \cdot 10^{-3}$ N KOH; 2) 3 hr after solution in 0.04 N KOH; 3) 3 hr after solution in 0.2 N KOH; 4) 1 hr after heating in 0.2 N KOH on a water bath.

The facts presented above compel us to assume the existence of two forms of the dihydroxobisdimethylglyoximocobalt(III) ion and, consequently, two forms of the bisdimethylglyoximodiaquocobalt(III) ion.

Absorption spectra at various pH were taken of the dihydroxobisdimethylglyoximocobalt(III) ion described in reference [10] and of the trisdimethylglyoximocobalt described by Nakahara [11] (Fig. 1). The similarity of the curves for these two compounds is immediately apparent, which leads to the conclusion that the three oxime groups in trisdimethylglyoximocobalt and the two oxime groups in the dihydroxo compound are similarly located. This means that in the dihydroxo compound the two hydroxyl groups are located cis to each other. This, in turn, forces us to assume that under the experimental conditions described in reference [10], i.e., heating in a strongly basic medium, the trans-dioximine $[Co(DH)_2AB]$ is converted to the cis-dioximine $[Co(DH)_2(OH)_2]^-$. This conclusion was confirmed by a spectrophotometric study of the changes which hydroxobisdimethylglyoximoaquocobalt undergoes in alkaline solution. To two 0.05-mmole portions of solid $[CoH_2O(DH)_2OH] \cdot H_2O$ was added 2 and 10 equivalents, respectively, of potassium hydroxide dissolved in 5.5 ml of water. These concentrated solutions were diluted to 50 ml before the spectra were determined.

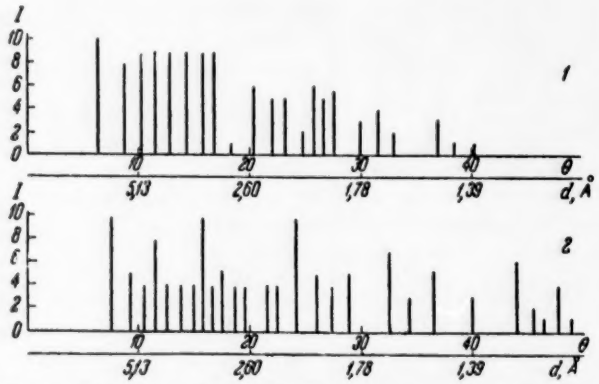

Fig. 3. Diagrams of the reflection angles and line intensities in the Debye patterns of dioximines of trivalent cobalt: 1) cis-$[Co(H_2O)_2(DH)_2]NO_3$, 2) trans-$[Co(H_2O)_2(DH)_2]NO_3 \cdot H_2O$.

As may be seen from the curves of Fig. 2, the trans form was converted to the cis form gradually at room temperature and rapidly upon heating. However, when the reaction mixture was heated, partial decomposition of the product occurred, as is evident from the height of the long-wavelength branch, 4.

The results of the spectrophotometric investigation were confirmed by synthesis of the salts of the cis and trans series. The reddish brown bisdimethyldiglyoximodiaquocobalt(III) nitrate has previously been described in reference [10]; this compound must have the cis configuration, according to the material presented above.

The trans-nitrate, $[Co(H_2O)_2(DH)_2]NO_3 \cdot H_2O$ was prepared from hydroxobisdimethylglyoximoaquocobalt by dissolving it in the required amount of 2 N HNO_3 and adding concentrated HNO_3 dropwise to the resulting solution, which was cooled during the addition. The yellowish brown precipitate was filtered onto a glass filter, and washed several times with cold water, alcohol, and ether. Microscopic examination showed that the nitrate was in the form of tetragonal prisms.

Found %: Co 14.31; 14.60; 14.48; N 17.19; 17.32

$[Co(C_4H_7O_2N_2)_2(H_2O)_2]NO_3 \cdot H_2O$. Calculated %: Co 14.54 N 17.28

The trans-bisdimethylglyoximocobalt perchlorate $[Co(H_2O)_2(DH)_2]ClO_4 \cdot 5H_2O$ was prepared by a similar route, and microscopic examination of this compound showed it to be in the form of long yellow tetragonal plates.

Found %: Co 11.20; 11.46-

$[Co(C_4H_7O_2N_2)_2(H_2O)_2]ClO_4 \cdot 5H_2O$. Calculated %: Co 11.45

The absorption curves of the latter two salts in acid media were in complete agreement with Curve 1 (Fig. 1). Figure 3 presents the Debye patterns of the cis- and trans-bisdimethylglyoximodiaquocobalt(III) nitrates.

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CATALYTIC DEHYDROGENATION OF CYCLOHEXANOL

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In previous communications [1], we have reported the results of investigations of the dehydrogenation of a series of aliphatic alcohols of different structures over a mixed oxide catalyst. It was shown that this catalyst promoted dehydrogenation of the alcohols without appreciable formation of byproducts from decomposition and dehydration of the alcohol. It was shown in the present work that this same oxide catalyst is active for the dehydrogenation of cyclohexanol. The dehydrogenation of cyclohexanol to cyclohexanone has been studied by numerous authors, since cyclohexanone has been widely used for the production of polyamide fibers and is also useful as a good solvent. Tur, Anisimov and Platonov [2] studied the dehydrogenation of cyclohexanol over finely dispersed rhenium, and they found that the yield of cyclohexanone is 25.3% at 350°. Benzene, cyclohexane, and other hydrocarbons were formed as byproducts. By dehydrogenation of cyclohexanol over a nickel aluminum catalyst at 380°, Zelinskii and Komarevskii obtained cyclohexanone in a yield of about 37% [3]; in addition, large amounts of benzene (~ 48%), phenol, cyclohexene, and polymeric products were formed. Dehydrogenation of cyclohexanol proceeds over zinc and copper catalyst at 400-600° [4]. Treshchanovich [5] compared the rates of dehydrogenation of cyclohexanol over iron-zinc catalysts of different compositions, and he found that the reaction rate was higher over the catalyst with the lower iron content (12.5%). According to the data of certain Japanese investigators [6], when cyclohexanol is passed at 350° over an alloy catalyst (a Raney type catalyst having a component ratio Cu : Al : Ni of 58 : 40 : 2) the cyclohexanol content of the catalyzate is 85%. However, data obtained by these same investigators [7] showed that the activity of the catalyst decreased to half after several hours, and after 400 hr it was only 20-30% of the initial activity.

The kinetics of the dehydrogenation of cyclohexanol were investigated in the present work. The relative adsorption coefficients of cyclohexanone and the reaction rate constants were determined, and the experimental data were used to calculate the activation energy, and the changes in free energy, heat content, and entropy during adsorptive displacement of the alcohol molecule by a cyclohexanone molecule from the active dehydrogenation centers. Moreover, dehydrogenation conditions required for good yields of cyclohexanone were determined.

EXPERIMENTAL

The experiments were carried out by a flow method in an apparatus which has previously been described [8]. The same sample of oxide catalyst was used in the experiments. The catalyst, 11 ml, was charged to a quartz tube having a diameter of 16 mm. The alcohol was fed by means of an automatically controlled apparatus. The cyclohexanol, which was distilled before an experiment, had the dollowing constants: b.p. 160.5°, d^{24}_4 0.9458, $n^{22}D$ 1.4660; literature values [9]: b.p. 160.5-161°, d^{30}_4 0.94155, $n^{25}D$ 1.4677.

The cyclohexanone used in the experiments in which the adsorption coefficients were determined was separated from the catalyzate obtained from the dehydrogenation of cyclohexanol; after distillation, the cyclohexanone had the following properties: b.p. 155.2-156°, d^{20}_4 0.9463, $n^{20}D$ 1.4545; literature values: b.p. 155.7°,

TABLE 1

Catalytic Dehydrogenation of Cyclohexanol

Temp., °C	H_2 obtained, in ml/5 min (STP)	Dehydrogenation, %	Temp., °C	H_2 obtained, in ml/5 min (STP)	Dehydrogenation, %
v = 1.2 ml in 5 min; theor. amt. H_2, 256.6 ml in 5 min			v = 1.4 ml in 5 min; theor. amt. H_2, 297 ml in 5 min		
264	20.0	7.9	269	24	8.1
269	28.0	11.0	281	42.8	14.4
281	48.1	18.9	300	82	27.6
297	72.5	28.4	317	123	41.5
302	85.0	33.4	322	140	47.2
313	108	42.4			
320	130	51.0			
330	160	62.9			

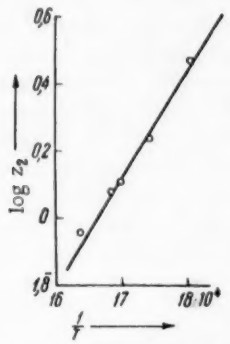

Fig. 1. Dependence of log z_2 on the reciprocal of the temperature.

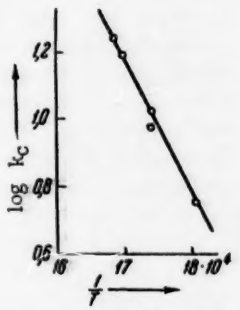

Fig. 2. Dependence of log k_c on the reciprocal of the temperature.

d^{20}_4 0.9465, $n^{19}D$ 1.4503. The catalyzate was analyzed for cyclohexanone content by reacting it with hydroxylamine hydrochloride. The effluent gas was pure hydrogen. The amount of ketone found by analysis and the hydrogen formed were in close agreement. The reaction rate was determined from the amount of hydrogen formed. Experiments with cyclohexanol were carried out over a temperature interval of 264 to 336° at alcohol feed rates, v, of 1.2 and 1.4 ml per 5 min. Conversion of the alcohol to cyclohexanone ranged from 16 to 75.8% of theoretical (Table 1). With the aim of determining the relative adsorption coefficients of cyclohexanone, dehydrogenation rates were measured with binary mixtures of cyclohexanol and cyclohexanone containing 24.6 mole % cyclohexanone. The experiments were carried out over the same temperature interval and at the same feed rates as the experiments with pure cyclohexanol. It may be seen from an examination of Table 2 that the relative adsorption coefficient of cyclohexanone was 3.03 at 281° and decreased to 0.91 with an increase in the temperature to 336°. The relationship between z_2 and the reciprocal of the absolute temperature was logarithmic. As may be seen from Fig. 1, the points lie on a straight line. The values of the relative adsorption coefficient of cyclohexanone remained unchanged when the feed rate was varied but the temperature was maintained the same (Table 2).

TABLE 2

Adsorptive Displacement Thermodynamic Functions

Temp., °C	Rel. adsn. coeff. z_2 (v = 1.2 and 1.4 ml per 5 min)	ΔF, cal	ΔH, kcal	ΔS, kcal per degree/mole
281	3,03	—1218		31,3
300	1,75	— 638,6	16,1	29,1
317	1,3	— 214,6		27,5
320	1,2			
336	0,91			

TABLE 3

Reaction Rate Constants and Activation Energy

Temp., °C	v, ml per 5 min	k_c, ml·min·ml	ϵ, kcal/mole	log k_0
281	1,2	1,16		
302	1,2	2,13		
320	1,2	3,5	18,2	7,24
300	1,4	9,62		
317	1,4	15,4		

TABLE 4

Cyclohexanone Yields and Catalyzate Compositions

Temp., °C	v, ml/liter/hr	Catalyzate composition, wt.%				Alcohol conversion, wt. %	Yield of cyclohexanone based on alcohol converted, wt %
		fraction boiling to 100°	cyclohexanone	cyclohexanol	dimer		
333	3180	—	66,2	32,1	1,7	67,9	97,4
342,5	3940	1,15	75,1	21,7	2,3	78,3	95,6
353	3940	1,7	79,0	16,5	2,8	83,5	94,4
360	3940	1,6	83,0	11,8	3,3	88,2	94,4

The reaction rate constants for the dehydrogenation of cyclohexanol were calculated by means of a previously presented [10] equation for monomolecular catalytic reactions in a flow system. The calculated values of the rate constant are shown in Table 3. When the logarithm of the rate constants was plotted against the reciprocal of the absolute temperature, the points fell on a straight line in accordance with the Arrhenius equation (Fig. 2). The activation energy calculated from the experimentally determined rate constants was 18.2 kcal/mole, and the logarithm of the preexponential factor, log k_0, was 7.24.

The thermodynamic functions of the adsorptive displacement, the changes in free energy, heat content, and entropy, were calculated from the experimentally determined values of the relative adsorption coefficient by the usual equation [8] (Table 2). Experiments carried out with cyclohexanol at higher temperatures showed that conversion of the alcohol increased from 67.9% to 88.2% when the temperature was increased from 333° to 360° and the alcohol feed rate was increased to 3.1-3.94 liters per liter of catalyst per hour. At the same time, the cyclohexanone yields were 97.4 and 94.4% of the alcohol reacted, respectively. 1-Cyclohexylidenecyclohexanone was simultaneously formed in an amount of 1.7 wt. % to 3.3 wt. % (Table 4). The catalyzate from the experiments was distilled, and the cyclohexanone content was determined. The 1-cyclohexylidenecyclohexanone was characterized by preparation of the oxime, which had an m.p. of 146-147°.

Found %: C 74.3; H 9.91

$C_{12}H_{18}NOH$. Calculated %: C 74.6; H 9.94

Thus, cyclohexanone can be obtained in good yields by dehydrogenation of cyclohexanol over an oxide catalyst at elevated temperatures and higher alcohol feed rates; hence, the method is of practical interest for the production of cyclohexanone.

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ON THE SIGNIFICANCE OF THE KINETIC ISOTOPE EFFECT IN THE THEORY OF HYDROGEN SUBSTITUTION IN AROMATIC SYSTEMS

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Translated from Doklady Akademii Nauk SSSR, Vol. 133, No. 3, pp. 581-584,
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In our study of the mechanism of substitution in aromatic compounds, we observed contradictions between the kinetic and isotopic data during iodination and bromination of benzene derivatives. In particular, it was found that the removal of a proton in the rate-controlling stage of the reaction and the appearance of a proton acceptor in the kinetic equation were not always associated with a kinetic isotope effect.

This is true for iodination of m- and p-dimethylaminobenzenesulfonic acid and m-dimethylaminobenzoic acid ions with iodine, bromination of the m-anisolsulfonate ion with hypobromous acid, and probably other cases also.

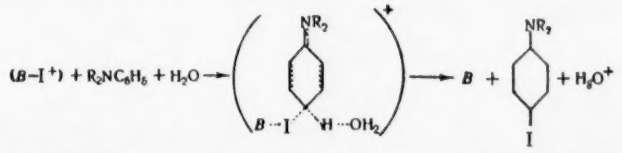
Thus, it was shown that the kinetic equation for the iodination of tertiary aromatic amines has the form:

$$-\frac{d(\mathrm{I})}{dt} = k \cdot M[\mathrm{I}^+] \cdot B + k' M[\mathrm{I}_2] B,$$

where (I) is the analytical concentration of iodine and M and B are the concentrations of the aromatic amine and the basic component of the buffer mixture, respectively, [1, 2]. Although this equation is equally applicable to all tertiary amines studied, the kinetic isotope effect, $i = k_H / k_D$, is different: i = 3 for dimethylaniline, while i varies from 1.8 to 1 for the m-dimethylbenzoate ion under different conditions; an isotope effect is absent (or very small) in the iodination of dimethylaminobenzenesulfonates.

An isotope effect is not associated with bromination of the m-anisolsulfonate ion with hypobromous acid, although the concentration of the base enters into the kinetic equation.

In analyzing these relationships, we first tended to assume that the base B enters into the composition of the iodinating complex [2, 3] and, consequently, that a typical scheme of the reaction has the form:

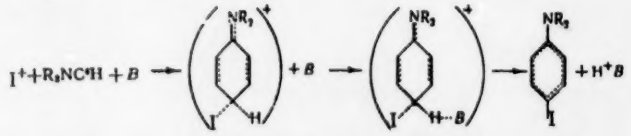


With this assumption, the presence or absence of a kinetic isotope effect depends on the stage in which a proton is split off by a molecule of water, and is not connected with the empirical kinetic equation of the reaction.

However, in a continuation of our investigation, we obtained evidence that the base B acts in the reaction as a proton acceptor, and not as a participant in the iodinating complex. Specifically, by introducing various

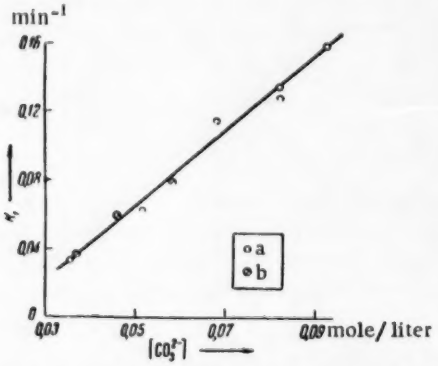
buffer salts into the mixture, we established that the iodination rate increases with an increase in the basicity and concentration of the basic component of the buffer solution. This also applies to the case where there is an isotope effect (aniline) and to the case where i = 1 (N,N-dimethylmetanilate ion). These data are presented in Fig. 1 for the iodination of the dimethylmetanilate ion [k_1 is the rate constant in the equation $d(I)/dt = k_1(I)$].

It follows from theoretical considerations that the strength of the halogenating agent is greater the less the basicity of the donor component of the active complex. Therefore, $(I^+ \ldots CO_3^{2-})$ should be weaker than $(I^+ \ldots HCO_3^-)$. In the pH interval indicated in the caption to Fig. 1, $[HCO_3^-] \gg [CO_3^{2-}]$, but the reaction proceeds through the CO_3^{2-} ion, and not through the HCO_3^- ion. This relationship and also the decrease in the isotope effect with an increase in the concentration of the CO_3^{2-} ion indicate that the base acts as a proton acceptor according to the scheme:



Evidently, the removal of the proton is the limiting stage of the reaction. As regards the isotope effect, it is present in some cases and absent in others. •

We found that during iodination of certain (but not all) compounds, the isotope effect can decrease and even disappear with an increase in the concentration and basicity of B, and, on the contrary, it can increase with an increase in the acidity of the solution. The decrease in the isotope effect with an increase in the basicity of the medium might well be associated with an acceleration of the stage in which the proton is split off; however, it must be remembered that in all cases B enters into the kinetic equation as a necessary component, and consequently, cleavage of the proton limits the over-all rate of the reaction.



Rate of iodination of the m-dimethylaminobenzoate ion as a function of the concentration of CO_3^{2-} ions in the pH interval 8.4 to 8.8 (30°). Concentrations, in mole/liter: $(I)_0$ 0.005; KI 0.3; M, 0.01; $[HCO_3^-] + [CO_3^{2-}]$): a) 1.05, b) 0.777.

These relationships can be explained on the basis of general principles by a superposition of equilibrium and kinetic relations, which act in opposite directions [4, 5]. However, these relationships do not follow simple and unequivocal rules. Thus, during iodination of aromatic amines we found a kinetic isotope effect varying from 3 to 4.8, both for extremely active compounds and for rather inert compounds. On the other hand, a kinetic isotope effect was not observed with certain amines of average activity [2]. It should be noted that primary amines substituted in quinogenic positions are iodinated three to four times more slowly than the analogous light compounds, while an isotope effect is absent during iodination of tertiary amino compounds. However, this rule is not followed in the case of dimethylaniline (i = 3).

The kinetic isotope effect is not directly connected with the activity of the halogenating agent. We confirmed this by brominating the m-anisolsulfonate ion with reagents of different strengths [6].

•It might well be assumed that the isotope effect disappears, because the splitting off of a proton takes place in two stages: the first, relatively slow stage is the formation of the complex $(Ar \ldots H \ldots CO_3^{2-})$ and this is followed by the relatively rapid stage in which the proton is split off in the form of HCO_3^-. However, this is contradicted by the fact that the tendency toward a decrease in i increases with an increase in the basicity of B. It would seem natural to expect the reverse relationship. Moreover, there is basis to assume that the deuterated compound should form a complex with B more difficultly than the hydrogen analog.

Agent	Br^+	Br_2	BrOH
Rel. act.	>1400	1	0.0015
i	1	2.6	1

Thus, there was no kinetic isotope effect when the strongest (BrOH) brominating agents were used. The isotope effect appeared when a brominating agent of average strength (elemental bromine) was used.

These peculiar relationships are undoubtedly associated with the different stages and migrations of the hydrogen atoms during the reaction, and for this reason the kinetic isotope effect is an interesting object for study. However, as the data of this work show, determinations of i give ambiguous results. and are not always effective when they are used as a method of establishing the mechanism of substitution in aromatic systems in the usual sense of the word. In particular, the absence of an isotope effect apparently does not permit one to form any reliable conclusion as to the succession and significance of the stages in substitution reactions of aromatic compounds.

From this point of view, it should be remarked that the results of the well-known experiments of Melander on the isotope effect during nitration and bromination of aromatic compounds [7] ($k_H/k_T = 1$) do not of themselves categorically prove that the splitting off of a proton does not limit the reaction rate. However, it was indicated earlier that the experiments of Melander are subject to a different interpretation [8] than that given by the author.

Experimental data (with the assistance of E. I. Tomilenko). The sodium salt of m-dimethylaminobenzoic acid was prepared from m-nitrobenzoic acid by simultaneous reduction and methylation [9]. The m-dimethylmetanilate was prepared by sulfonation of dimethylaniline [10]. The m-anisolsulfonate was prepared by methylating the m-phenolsulfonate salt with dimethyl sulfate and purification of the product through m-anisolsulfonyl chloride [11].

TABLE 1

C	k_1, min^{-1}	k/C
0.0825	0.0368	0.447
0.133	0.0622	0.467
0.165	0.0783	0.474
		0.46

In parallel experiments, i = 3.4.

The 2,4,6-trideutero-m-dimethylmetanilic acid was prepared by means of H-D exchange between the light amino compound and a 15-17% solution of DCl, which was prepared from 98-99% D_2O and $SOCl_2$. H-D exchange between the light compound and D_2O could not be used for the preparation of 2,4,6-trideutero-m-anisolsulfonate and 2,4,6-trideutero-m-dimethylaminobenzoic acid, since some side reactions occurred during the prolonged heating in an acid medium. Therefore, they were prepared from previously deuterated m-phenolsulfonate and m-aminobenzoic acid. Determination of D in the water obtained by combustion of the deutero compounds was carried out by the falling drop method [12].

In the kinetic experiments, iodination of the amines was carried out in solutions of iodine in potassium iodide at 25° or 35° (± 0.05°), both in the presence and in the absence of buffer salts. The analytical concentration of the iodine was determined by titration of a sample with thiosulfate solution in small volumes. Control experiments showed that over the pH range studied, formation of iodate was insignificant.

The concentrations of CO_3^{2-} shown in Fig. 1 were calculated from the over-all concentrations of carbonates in the experiment using the second dissociation constant of carbonic acid, which is $1.5 \cdot 10^{-10}$ at the average ionic strength of our solutions [13]. The hydrogen ion concentration required for the calculations was determined in a test mixture with a glass electrode. In the pH interval 8.4 to 8.8, the concentration of HCO_3^- ion was almost equal to the over-all concentration of carbonates in the solution, and the reaction rate was proportional both to $[CO_3^{2-}]$ and to $[OH^-]$. However, experiments carried out at constant concentration of CO_3^{2-} ion at different pH values showed that the hydroxyl ion concentration had no significance with respect to the mechanism of the reaction. In parallel experiments with the same component concentrations, 2,4,6-trideutero- and ordinary m-dimethyl aminobenzoate ions underwent iodination at equivalent rates. In a similar reaction, bromination of m-anisolsulfonate ion with hypobromous acid, the rate constant (at 0°) increased from 0.177 in the absence of a buffer to 0.41 liters/mole/minute in the presence of carbonate at a concentration of 0.5 M and a pH of 8.5. In both cases i = 1.

TABLE 2

Compound	% H-D exchange	M, mole/liter	Buffer, mole/liter	pH	k
m-Dimethylamino-benzoate ion	98	0.01	Acetate, 0.16	4.5	1.8
		0.02	–	(8-5)	1.3
		0.01	Phosphate, 0.35	8	1.2
		0.01	Carbonate, 1.6	8.8	1.0
m-Dimethylamino-sulfonate ion	97.2	0.06	HCl, 50% neutralization	3.5	1.2
		0.01	–	(7-5)	1.0
		0.01	Phosphate, 0.3	8	1.0
Aniline	96.6	0.02	–	(8-5)	3.5
		0.04	Phosphate, 0.38	7.0	3.4
		0.012	Carbonate, 1.0	9.4	3.4

Table 1 presents values of the rate constant for the iodination of aniline at a pH of 9.6 to 9.7 and different concentrations of carbonate. The concentrations of the rest of the reagents were, in mole/liter: (I), 0.005; KI, 0.4; aniline, 0.025; C denotes the sum $[HCO_3^-] + [CO_3^{2-}]$. The data of Table 1 show that the reaction rate is proportional to the concentration of buffer salt (as a matter of fact, essentially to the content of its more basic component.)

Table 2 presents data on the change of i values during iodination of amines as a function of the pH of the medium.

The deutero analogs of the compounds indicated in Table 2 contained D in the 2, 4, and 6 positions; $(I)_0$ = 0.005 M; temperature 25 or 30°.

The isotope values obtained under the various conditions were reproduced well in repeated experiments.

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•Original Russian pagination. See C. B. translation.

SYNTHESIS OF CERTAIN 8,9-PENTAMETHYLENEPURINES

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(Presented by Academician M. M. Shemyakin, March 9, 1960)
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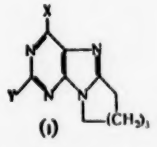
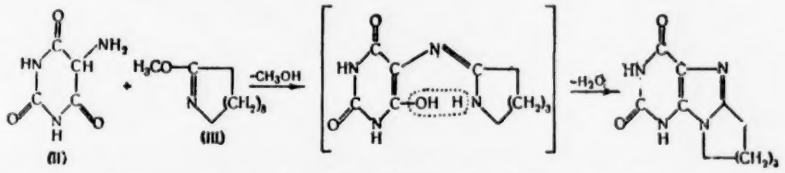
The presence of purine compounds in nucleic acids as well as the high biological activity of 6-substituted purines and of alkaloids of the dihydroxypurine series have recently stimulated considerable interest in the synthesis of purine derivatives, including compounds with a tricyclic system containing a purine nucleus [1, 2]. This induced us to synthesize for biological study certain representatives of the new purine series, 8,9-polymethylenepurines, and we elected to start with derivatives of 8,9-pentamethylenepurine (I, n = 3):



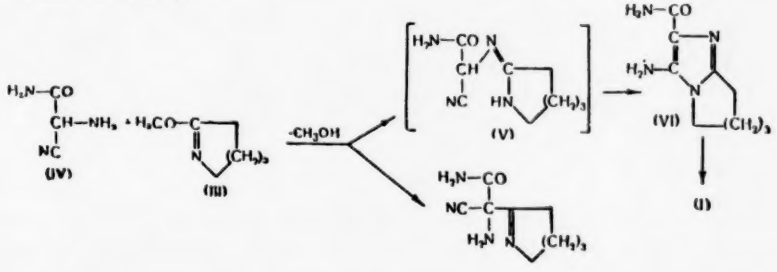
(I)

Our immediate problem was to prepare structural analogs of such biologically important purines as adenine guanine, kinetin (6-furfurylaminopurine), 6-mercaptopurine, etc. With this aim, we attempted to carry out the synthesis of I by condensation of uramil (II) with O-methylcaprolactim (III):



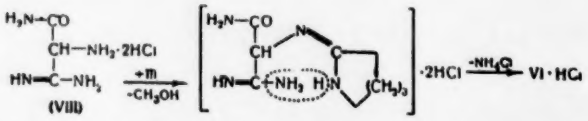
(II) (III)

However, in a series of attempts to condense II with III under different conditions, we were unable to obtain any interaction, and the II and III were completely recovered in all cases. In further attempts to accomplish the synthesis of I, another promising variant was studied; this variant consisted in the condensation of III with α-amino-α-cyanoacetamide (IV):

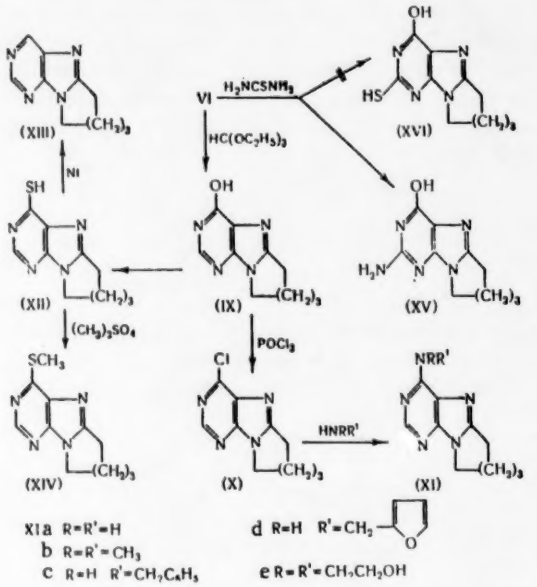


(IV) (III) (V) (VI) (I)

When III was heated with IV in Ethyl Cellosolve for a short time (Method A), a substance with an m.p. of 272-274° (with decomposition) was obtained; since it is possible for III to condense with IV at the amino group of the latter and since III can also react with compounds having an active CH_2 group [3], it was possible that the structure of this substance was that of one of the three isomeric compounds V, VI, and VII. When the condensation of III with IV was carried out in boiling alcoholic HCl, a hydrochloride with an m.p. of 257-259° was obtained. This same hydrochloride was also prepared from aminomalonamidoamidine dihydrochloride (VIII) [4] by heating with III:



The same base with an m.p. of 272-274°, which was also identical with the substance prepared by Method A, was obtained from these two hydrochlorides. The infrared spectrum of this substance showed that it contained no CN group, but absorption bands characteristic of NH_2 and H_2NCO groups (2.95, 3.04, 3.15, and 6.12 μ) were present. Thus, structures V and VII must be discarded as possible structures of the product of the condensation of III with IV, leaving only structure VI. Conclusive proof of the structure of this compound as the amide of 1,2-pentamethylene-5-aminoimidazole-4-carboxylic acid was obtained by a series of conversions of VI to various derivatives of 8,9-pentamethylenepurine (see scheme and Table 1).



Substance	IX	X	XIa	XIb	XIc	XId	XIe	XII	XIII*	XIV	XV
M.p., °C	308–311 (decomp.)	141–143	226,5–228,5	142–144	153–155	168–170	177–179	290–292 (decomp.)	99–101	139–141	>360

*M.p. of picrate, 166-169°.

The ultraviolet spectra of IX and XII proved to be identical to the spectra of hypoxanthine and 6-mercaptopurine. It is interesting to note that fusion of VI with thiourea gave 8,9-pentamethyleneguanine (XV), which had an ultraviolet spectrum corresponding to that of guanine, in place of the expected XVI.

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*Original Russian pagination. See C. B. translation.

4-CYCLOPENTENE-1,3-DIONE

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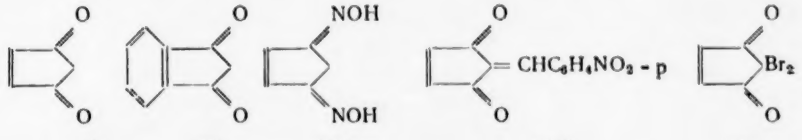
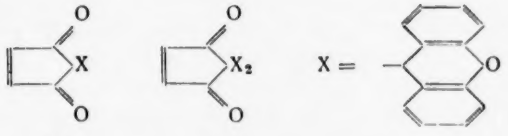
The preparation of 4-cyclopentene-1,3-dione was briefly described in 1957 [1], and a more detailed description was published in 1959 [2].

Since I is perhaps the simplest analog of 1,3-indanedione (II), it seemed to us desirable to study more closely the properties of this compound. We modified somewhat the method of the above reference, and developed a more convenient method for the preparation of I. Through the use of silver chromate, which possesses both dehalogenating and oxidizing properties [3], we were able to convert 3,5-dibromo-1-pentene directly to I. This yellow substance (m.p. 36-37°) is extremely unstable toward alkaline reagents, forms a dioxime (III) in the usual manner, condenses with p-nitrobenzaldehyde to yield IV, and gives V upon bromination. We were unable to add bromine across the double bond. The action of a base on V readily split out the bromine, and V liberated iodine from KI. Catalytic hydrogenation in the presence of skeletal nickel converted both I and V to 1,3-cyclopentanedione [4, 5].



(I) (II) (III) (IV) (V)



(VI) (VII)

In 1897, Wolff [6] reported the preparation from dibromolevulinic acid of a compound to which he ascribed structure V. We repeated this synthesis and found that the substance prepared by Wolff differs greatly from V, and, judging by its properties and infrared spectrum (Table 1), it does not have structure V; it is possible that it has a lactone structure [7, 8].

It was not possible to acylate or alkylate I, but condensation of I with xanthydrol proceeded readily; this reaction is characteristic of β-diketones [9, 10], including 1,3-indanediones [11-13]. Xanthylation of I with an equimolar amount of xanthydrol gave both the monoxanthyl (VI) and the dixanthyl (VII) derivatives. The xanthyl groups were easily removed from VI and VII by the action of bromine.

TABLE 1

Infrared Spectra of 4-Cyclopentene-1,3-dione and Its Derivatives

Compound	State	$-NO_2$		>C=C<, >C=N–	>C=O	Region of 3000–3700 cm^{-1}
I	Solid[1]					~3390 (weak)
	In CH_2ClCH_2Cl				1715 (98)	Not taken
	$8{,}3 \cdot 10^{-2}$ M	—	—	—[2]	1752 (38)	
	in CCl_4[3]				1718 (61)	—[4]
	$2{,}3 \cdot 10^{-2}$ M	—	—	—		
	in CCl_4[3]				1718 (92)	—[4,5]
	~$4 \cdot 10^{-2}$ M	—	—	—	1751 (19)	
VI	Solid[7]		1576 (51)			
			1603 (36)	—	1695 (93)	—
	In CH_2ClCH_2Cl[7]		1580 (29)			
	$4 \cdot 10^{-2}$ M	—	1605 (25)	—	1712 (79)	—
VII	Solid[7]	—	1577 (44)			
			1599 (37)	—	1695 (84)	—
	In CH_2ClCH_2Cl[7]		1580 (29)			
	~$4 \cdot 10^{-2}$ M	—	1602 (31)	—	1704 (67)	—
Xanthydrol	Solid[7]	—	1579 (37)			
			1608 (40)	—	—	Not taken
III	Solid[6]	—	—	1637 (74)	—	~3090 (50)
						~3180 (55)
						~3374 (40)
IV	Solid	1509 (77)	1595 (72)	1622 (77)	1689 (90)	
					1736 (43)	Not taken
2-p-Nitrobenzal-1,3-indanedione	Solid	1519 (84)	1593 (69)	1628 (65)	1692 (93)	
					1734 (50)	Not taken
V	Solid[6]	—	—	~1559 (62)	1692 (28)	—
	In CH_2ClCH_2Cl[6]			1616 (68)	1731 (48)	Not taken
Bromination product	$3 \cdot 10^{-2}$ M	—	—	~1643 (37)[8]		
Wolff [6]	Solid[6,7]	—	—	1548 (86)	1767 (96)	~3110
					1789 (87)	(average)

[1] Taken in the interval of 1490-1820 cm^{-1}. There was almost monotonic absorption to about 1760 cm^{-1}; consequently, it was impossible to distinguish individual bands. [2] Using an IKS-14 double beam instrument, weak bands were observed at 1646 and 1565 cm^{-1} in the spectrum of a concentrated solution of I. [3] Owing to the range of absorption of the solvent, the interval from 1600 to 1820 cm^{-1} was available. [4] Taken in the interval from 2500 to 3700 cm^{-1}. [5] At higher concentrations of I, there was a weak band at about 3400 cm^{-1}. [6] Taken in the interval from 1490 to 1830 cm^{-1}. [7] These spectra were taken using a less sensitive instrument than was used in the remaining cases, and some of the weaker bands may have been missed. [8] Melt.
Note: All spectra were taken with an IKS-12 single beam instrument with an NaCl prism, in the majority of cases in the intervals from 1490 to 1760 cm^{-1} and 3000 to 3700 cm^{-1}. The solid compounds were suspended in paraffin oil. The frequencies are reported in reciprocal centimeters; the figures in parentheses are the intensities in percent absorption.

The infrared spectra of I in CH_2ClCH_2Cl and in CCl_4 were obtained (Table 1). In both cases, bands due to valence vibrations of the carbonyl groups (1715 cm^{-1} and 1718 cm^{-1}) were found; these lie within the limits reported for the cyclopenten-2-one-1-carbonyl frequencies [14-17]. The increase in the carbonyl frequency when the medium was changed from CH_2ClCH_2Cl to the less polar CCl_4 conforms to the general rule [18, 19]. A second band at 1752 and 1751 cm^{-1} was of low intensity, and was due to interactions of the vibrations of the two carbonyl groups [20]. No band due to valence vibrations of the double bond were observed in the spectrum of I, probably owing to the high symmetry of the molecule with respect to the double bond, which makes the vibrations less intense. Only when concentrated CH_2ClCH_2Cl solutions were used and a double-beam instrument was employed were the two weak bands at 1646 and 1565 cm^{-1} found. The latter of these two bands can probably be assigned to double bond vibrations [21-24].

TABLE 2

Ultraviolet Spectrum of I

Solvent	K band	
	λ_{max}, mμ	ε
Hexane	217.5	12220
C_2H_5OH (95%)	218.5	12280
Water	221.5	12900

The infrared spectrum of the dioxime (III) excluded the possibility that the NH_2OH had added across the double bond [25]. The spectrum of solid III did not contain a carbonyl frequency; only a band at 1637 cm^{-1} was found, and this can be assigned to the conjugated C = N bond. Two carbonyl bands at 1689 cm^{-1} (stong) and 1736 cm^{-1} (weak), a band due to conjugated double bond vibrations at 1622 cm^{-1} [20, 26], a band at 1595 cm^{-1} which belongs to the aromatic ring [20, 26-28], and a band at 1509 cm^{-1}, which apparently could be assigned to antisymmetric vibrations of the nitro group [29, 30] were all observed in the spectrum of solid IV. The spectra of the structurally similar 2-benzal- [20] and 2-p-nitrobenzal-1,3-indanediones are similar. In the spectrum of IV, in which there is an additional conjugated bond, the carbonyl frequency was lower by 6 cm^{-1} in comparison to the 2-substituted derivatives, for example, VI and VII [16, 20, 26].

The infrared spectrum of solid V showed a strong decrease in the carbonyl group and double bond frequencies, but the normal values were observed when the spectrum was taken in CH_2ClCH_2Cl. The band at 1731 cm^{-1}, which is due to the carbonyl groups of V, was higher by 16 cm^{-1} than the corresponding band in the spectrum of I. It is interesting that this difference has been found in the spectra of analogous compounds with cyclopentanone and cyclopentenone systems [31-33, 15]. In contrast to I, a still more intense band at 1616 cm^{-1} was observed; this is assigned to the double bond. The reason for the appearance of such a highly intense band is not clear. The origin of another, less intense band in the form of a shoulder at 1643 cm^{-1} is also not clear [34].

The infrared spectra of VI and VII confirmed their structures. The carbonyl bands of these two compounds appeared at the same frequency, 1695 cm^{-1}, in the spectra of the solid forms. However, in CH_2ClCH_2Cl, they differed: 1712 cm^{-1} (VI) and 1704 cm^{-1} (VII). The slight decrease in the frequency in VI as compared to the corresponding band for I (1715 cm^{-1}) is normal and is connected with the introduction of an additional alkyl substituent, which usually decreases the carbonyl group frequency [35, 36]. The comparatively low position of this frequency in the spectrum of VII is probably due to steric hindrance [35, 36]. Moreover, in the spectra of VI and VII, both solid and in solution, there were still other bands; these were connected with the xanthyl groups, since they appear in the spectrum of xanthydrol.

Except for references [1, 2], the literature contains no data on the question of keto–enol equilibrium in 4-cyclopentene-1,3-diones. Certain conclusions may be formed on the basis of a study of the spectra of these compounds. Only normal, unshifted frequencies belonging to the diketo form were found in the spectra of I, VI, and VII. The band at about 1750 cm^{-1} also belonged to the diketo form. Other bands which might have been associated with a possible enol form were not observed. The weak band at 1646 cm^{-1}, which was found in the spectrum of the concentrated solution of I in CH_2ClCH_2Cl, cannot be ascribed to the enol form, because it could originate only in the case of dissociation of I or as a harmonic (a weak band at 816 cm^{-1} was observed in the spectrum of solid I).

The absence of an enol form is also confirmed by the spectra of I, VI, and VII in the region of OH group valence vibrations. No bands were found in this region in the spectra of VI and VII, and the low-intensity band in the spectrum of I was probably a harmonic of the carbonyl frequency [37], because it remained in the spectrum of the CCl_4 solution, where enolization of I is impossible. An analogous conclusion follows from a consideration of the u.v. spectra of I, in which there was found only one intense band at about 220 mμ, which has been assigned to the K band of the 2-cyclopenten-1-one system [38, 39]. The shifting of this band depending on the solvent conforms to the general rule [40, 41].

Consequently, the 4-cyclopenten-1,3-dione system is not tautomeric and is a new member of the series of nonenolizable β-diketones, to which the 1,3-indanedione system obviously also belongs.

4-Cyclopentene-1,3-dione (I). To the mixture obtained by bromination of 22.6 g of cyclopentadiene with 17.4 ml of bromine in hexane was added 50 ml of acetone, and the solution was slowly added, with stirring, to a suspension of 150 g of silver chromate in 250 ml of 80% acetic acid at 28-30°. A solution of 25 g of CrO_3 in 50 ml of 80% acetic acid at this same temperature was then added, and the reaction mixture was stirred until the temperature began to drop. On the following day, the precipitated AgBr and Ag_2CrO_4 were filtered off and washed with acetone, water was added to the filtrate, and the filtrate was repeatedly extracted with ether. The ethereal extract was concentrated under vacuum. Ether was added to the dark residue. This was filtered, and hexane was added to the filtrate. When this solution was cooled (to below 50°), the I crystallized. The yield was 3.14 g (9.5%) after a second crystallization; m.p. 36-37°.

Dioxime (III). A solution of I and NH_2OH in aqueous alcohol was prepared at room temperature. The product was in the form of white crystals (from alcohol plus hexane); m.p. 243-245° (with decomposition).

Found %: N 22.33. $C_5H_6O_2N_2$. Calculated %: N 22.22

Xanthylation of 4-cyclopentene-1,3-dione. A solution of 0.12 g of I and 0.26 g of xanthydrol in 5 ml of a mixture of glacial acetic acid and alcohol (1 : 1) was allowed to stand at room temperature. After 3 to 5 days crystals separated, and these were boiled with alcohol. Yellow crystals of VI precipitated from the filtrate; m.p. 191-192° (with decomposition) (second crystallization from alcohol). The yield was 0.16 g (44%).

Found %: C 78.18; H 4.37
$C_{18}H_{12}O_3$. Calculated %: C 78.25; H 4.38

The residue on the filter (0.05 g) was recrystallized from acetic acid; the resulting yellow crystals of VII melted at 241-242° (with decomposition). When large amounts of xanthydrol were used, mainly VII was obtained. Xanthylation of VI also gave VII.

Found %: C 81.47; H 4.66
$C_{31}H_{20}O_4$. Calculated %: C 81.53; H 4.42

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COPOLYMERIZATION OF DIETHYLENAMIDES OF PHOSPHORUS ACIDS WITH BIFUNCTIONAL ORGANIC COMPOUNDS

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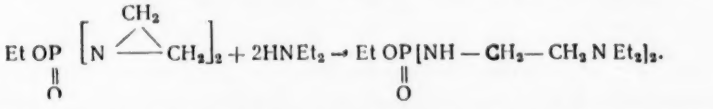
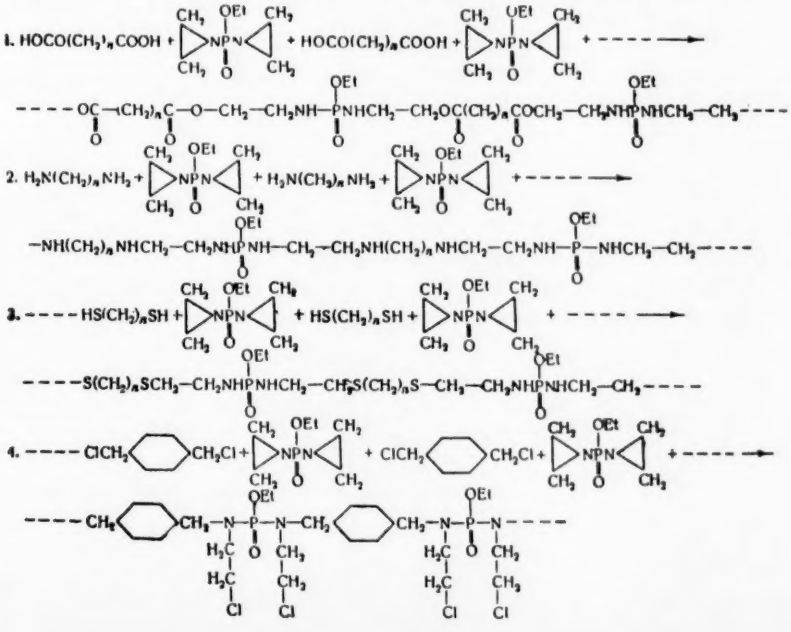
Our previous publications [1-3] have described the N-phosphonaminoethylation of organic compounds.

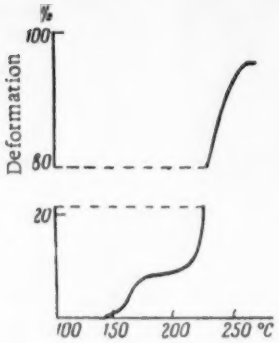
This reaction comprises the addition of ethylenamides of phosphorus acids, with opening of the ethylenimine ring, to various organic compounds containing suitable functional groups: NH_2, HNR, SH, OH, CH_2Cl, COOH, etc.

It has recently been shown [4] that ethylenamides of phosphorus acids also undergo this reaction at both ethylenimine groups, the addition being accompanied by opening of both rings, for example:



The occurrence of this reaction led us to believe that it would be possible to prepare linear copolymers with phosphorus-containing chains, by the interaction of diethylenamides of phosphorus acids with bifunctional organic compounds possessing the groups mentioned above—diamines, dicarboxylic acids (or dibasic inorganic acids), dimercaptans, etc. This reaction may be schematically represented as follows:





Alternation of the atoms in these chains may be considered reasonably well established on the basis of earlier investigations of the monomeric reaction.

Our experiments showed that diethylenamides of phosphorus acids actually do copolymerize with dicarboxylic acids, diamines, p-dichloromethylarenes, and other bifunctional compounds. Thus, for example, when equimolar amounts of isopropyl N,N'-diethylenamidophosphate and sebacic acid were heated at 110-120°, there was an exothermic reaction which resulted in the formation of a rubbery substance with a high percentage elongation.

Copolymerization of ethyl N,N'-diethylenamidophosphate with benzidine (in equimolar amounts) by heating at 125-130° was exothermic and resulted in the formation of a transparent solid polymer having the color of strong tea. An investigation of the thermomechanical properties (with an apparatus of the type constructed by B. Ya. Teitel'baum and M. P. Dianov) of the latter polymer showed that the viscoelastic state exists over the temperature interval of 150 to 220° (figure). At 300°, in the viscous flow region, the polymer could be drawn into filaments.

A series of other experiments was carried out, and all experiments resulted in polymeric materials; an investigation of these materials is currently under way. The ability of diethylenamides of phosphorus acids to add to functional groups of organic compounds may be used for the preparation of graft and block copolymers containing phosphorus. It is possible to form block copolymers with: 1) Polyamide chains, regardless of the nature of the terminal groups, since amide and carboxyl groups undergo the N-phosphonaminoethylation reaction equally well; 2) polyester chains having carboxyls as the terminal groups.

In a similar manner, monoethylenamides of phosphorus acids can be used to graft phosphono groups to the active ends or to branches of polymer molecules. Experiments carried out along these lines also led to positive results.

Simultaneous polymerization and polycondensation of sebacic acid (1 mole) with tetramethylene glycol (0.9 mole) and ethyl N,N'-diethylenamidophosphate (0.1 mole) gave an opaque, waxy polymer with a low melting point (about 60°.) The reaction was carried out by heating to 180° at atmospheric pressure (and to 230° under vacuum.)

The amide polymerization-polycondensation of sebacic acid (1 mole) with benzidine (0.9 mole) and ethyl N,N'-diethylamidophosphate (0.1 mole) by heating in a stream of nitrogen to 220° gave opaque, solid, horny polymers. The physicomechanical properties of these polymers are under study.

Thus, we now have a new method for the preparation of phosphorus-containing polymers through the use of the N-phosphonamino ethylation reaction.

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ABSORPTION SPECTRA OF DERIVATIVES OF 4-NO_2-DIPHENYLAMINE

THE EFFECTS OF ELECTRON-DONOR GROUPS IN THE META POSITION AND OF ALKYLATION OF THE NH GROUP

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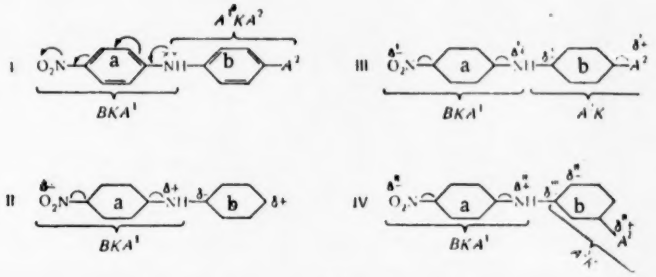
A study of the spectra of 4-NO_2 derivatives of diphenylamine (DPA) [1], structure (I), based on the principle of dividing the structure into individual chromophore components [2-4] led to the conclusion that "a single conjugated system (with participation of the p-electrons of the NH) with a single excitation vector along the π-system is absent."



There are two unconnected systems BKA^1• and A^1KA^2 (I) with their own laws for transition to the excited state. We observed the bands due to these systems in the spectra of (I). The vectors intersecting at the central N atom (which is a conjugation isolator) thus prove to be interconnected–dependent on each other to a certain extent [1]. Owing to disruption of coplanarity in (V),•• the N atom of the NH(NR) group can conjugate with either a or b. Thus, the existence of geometrical conjugation isomers is possible [7], and this may explain the chromophoric isomerism of NO_2 derivatives of DPA(see page 838).

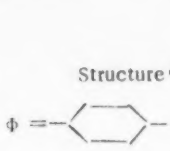
The basic chromophore system is BKA^1 (I), modified to some extent chiefly by polar shifts and by an excited state resulting from the effect of the A^2K. According to the rule connecting the bathochromic effect with the degree of electronic shifts,••• the greater the degree of electron shifting in BKA, p-$O_2N\Phi N<$, away from the state

•B is an electrophilic chromophore component (NO_2); K is a conjugated system; A, A^1, and A^2 are electron-donor chromophore components.

••Construction of the above representation of V took into account standard dimensions based on coplanarity [5]. The broken line indicates an H atom. The planes of the benzene nuclei, a and b, are tilted at an angle of about 33° [6]. In the case of NMe, this angle should be greater.

•••This rule was stated as early as 1915 by Ismail'skii as a consequence of the connection between color and the meso structure [7, 8], and was later restated by Lewis and Calvin [9].

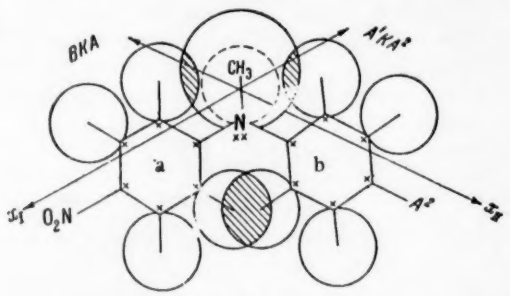
Spectra of the Compounds in 95% Ethanol

Compound No.	Structure•• Φ =  or C_6H_5	Bands of the system BKA				Bands of the system A^1KA^2 or KA^2			
		band x•••		band x'•••		band β		band γ	
		λ max, mμ	ε max	λ max, mμ	ε max	λ max, mμ	ε max	λ max, mμ	ε max
1	$O_2N\Phi NH\Phi$	395	29220	—	—	257	13500	—	—
2	$O_2N\Phi NHC_6H_4OMe$-	393	30430	—	—	257	17840	~220	~28240
3	$O_2N\Phi NHC_6H_4NHAc$-	395	28248	—	—	~260	~17720	245	29530
4	$O_2N\Phi NHC_6H_4N(Ac)_2$-	388	30230	—	—	254	18130	~220	~22300
5	$O_2N\Phi NHC_6H_4NH_2$-	399	28345	—	—	~260	~15760	235	31720
6	$O_2N\Phi NHC_6H_4NMe_2$-	403	24110	—	—	—	—	247	28740
7	$O_2N\Phi N$ (Me) Φ	387	21760	228,5	8425	250	5925	—	—
8	$O_2N\Phi N$ (Me) Φ OMe	388	22200	—	—	~250	~10430	222	17390
9	$O_2N\Phi N$ (Me) Φ NHAc	391	26090	—	—	~275	~11595	236	21015
10	$O_2N\Phi N$ (Me) Φ NH_2	397	21015	—	—	249	13720	235	13575
11	$O_2N\Phi N$ (Me) Φ NMe_2	397	18980	~245	~11110	265	17592	—	—
12	$O_2N\Phi N$ (Et) Φ	392	20694	228	8820	~250	~ 5880	—	—
13	$O_2N\Phi N$ (Et) Φ OMe	394	23300	—	—	~245	~ 7500	225	12950
14	$O_2N\Phi N$ (Et) Φ NHAc	394	23710	(220)	(27310)	~260	~10196	~230	~20078
15	$O_2N\Phi N$ (Et) Φ NH_2	400	21590	(~220)	(~47410)	250	13242	—	—
16	$O_2N\Phi N$ (Et) Φ NMe_2	401	19450	~240	~10650	265	16650	—	—
17	$O_2N\Phi N$ (Pr) Φ	391	20370	228	7450	~250	~ 5646	—	—
18	$O_2N\Phi N$ (Pr) Φ OMe	392	21898	(~220)	(58750)	254	8524	—	—
19	$O_2N\Phi N$ (Pr) Φ NHAc	392	22330	—	—	~270	~ 8980	237	18050
20	$O_2N\Phi N$ (Pr) Φ NH_2	400	25000	(~220)	(~51710)	~250	~15089	—	—
21	$O_2N\Phi N$ (Pr) Φ NMe_2	400	20260	~245	~11400	265	17700	—	—
22	$O_2N\Phi N$ (iso-Pr) Φ	390	22990	230	8935	~250	~ 4635	—	—
23	$O_2N\Phi N$ (iso-Pr)ΦOMe	390	24530	(~220)	(~62000)	~245	~ 9160	—	—
24	$O_2N\Phi N$ (iso-Pr)Φ NHAc	390	22700	—	—	—	—	242	20810
25	$O_2N\Phi N$ (iso-Pr)Φ NH_2	397	21950	(~225)	(~29480)	~250	~13950	—	—
26	$O_2N\Phi N$ (iso-Pr) Φ NMe_2	400	23088	~240	~11900	265	20410	—	—
27	$O_2N\Phi N$ (Me) C_6H_4OMe-	390	28000	—	—	~245	~ 9150	225	23610
28	$O_2N\Phi N$ (Me) C_6H_4NHAc-m	390	25250	—	—	—	—	242	26130
29	$O_2N\Phi N$ (Me) $C_6H_4NH_2$- m	395	27560	—	—	—	—	235	24070
30	$O_2N\Phi N$ (Me) $C_6H_4NMe_2$-m	395	26080	—	—	—	—	255	23620

• The spectra of Nos. 1-6 and 27-30 were taken at a concentration of 10^{-4}. The remaining spectra were taken at a concentration of 10^{-3}. ~ λ_{max} was determined approximately from the inflection in the curve; values of λ and ε in parentheses are for bands whose origins are still not clear.

••Me = CH_3; Et = CH_2CH_3; Pr = $CH_2CH_2CH_3$; iso-Pr = $CH(CH_3)_2$; Ac = CH_3CO.

•••Subdivision of the bands of the BKA system into x and x' is in the sense of references [9, 11].



V

corresponding to the limiting valence structure of Formula (I), the lower will be the energy required for excitation by light, and the greater will be the bathochromic effect. From this point of view, the cause of the bathochromic effect upon a change from p-$O_2N\Phi NH_2$ λ_{max} 371 mμ, to p-$O_2N\Phi NHC_6H_5$ λ_{max} 395 mμ ($\Delta\lambda$ + 24 mμ in ethanol and + 34 mμ in cyclohexane) must be sought in the increase in electronic shifts and the $\Delta+$ charge on the N atom in the system $O_2N\Phi N <$ (II) as a result of the effect of polar deformation of benzene ring b (II) (δ increases deformation). The effect of a phenyl group proved to be quite close to that of an alkyl group, as is apparent upon changing

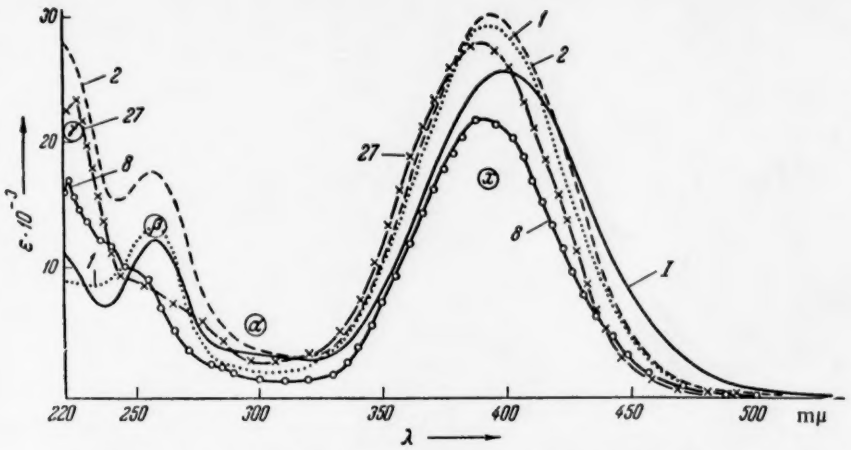


Fig. 1. 1, 2, 8, and 27) see Table 1; I) p-$O_2N\Phi NH\Phi OCH_3$-p'.

from p-$O_2N\Phi NH_2$ to p-$O_2N\Phi NMe_2$ (λ_{max} 390 mμ) and p-$O_2N\Phi NE_2$ (λ_{max} 400 mμ). Hence, it would be expected that the greater the electron-donor activity of the A^2 group in (III), the greater the polarization of the A^2K system, and the greater will be δ' (III); hence, the greater will be Δ'+ on the NH and the greater will be the bathochromic effect: H < $NHCOCH_3$ < OCH_3 < NH_2 < NMe_2 (Δλ = 0, + 2, + 5, + 10, + 15) [1]. Thus, our former conclusions have been confirmed [10]. These Δ λ effects were significantly lower than they would have been (+ 40 to + 120 mμ) had the conjugated chain actually been increased by four π electrons. Conjugation of p-A^2 with NO_2 is prevented by the lack of coplanarity [5]. The problem of the present investigation was to confirm the effect of A^2 in the meta position (IV) on the spectrum, and to explain the effect of further disruption of coplanarity by the introduction of an alkyl into the NH group on the spectrum of p-A^2- and m-A^2-substituted (V) (Table 1).

According to calculations based on molecular diagrams, the electronic charge at the m-C of $C_6H_5NH_2$ is lower than at the p-C at the C atoms of an unsubstituted benzene ring [12]. Therefore, it would be expected that in the case of meta derivatives of IV we would observe hypsochromic effects, since δ''' - < δ - < δ' -. Actually for m-A^2 = H, OCH_3, $NHCOCH_3$, $N(COCH_3)_2$, NH_2, NMe_2 Δλ = 0, - 2, 0, -7, + 4, + 8 mμ (Table 1, Nos. 1-6). Thus, the presence of a negative effect clearly stands out for m-OCH_3 and m-$N(COCH_3)_2$. However, the effects are positive (+ 4 and + 8) for strong donors (m-NH_2 and m-NMe_2), although from a study of the molecular diagrams using the molecular orbital method a negative effect would be expected [12].

If the above concept of the effect of the value of the δ''' charge on the value of the Δ''' + (IV) and on the spectra is correct, it would follow that: 1) in the case of such strong donor groups as NH_2 and NMe_2, the over-all electron density in benzene ring b is so greatly increased that in the position meta to NH_2 and NMe_2 there is a greater electronic charge than in the unsubstituted benzene ring of (III), i.e., in the case of NH_2 and NMe_2 δ''' - > δ -; 2) according to our spectroscopic data, the calculations of the electronic charges in the molecular diagrams of $C_6H_5NH_2$ are not sufficiently accurate (the difference in the values calculated by the molecular orbital method and by the mesomerism method also indicate this) [12]. On the other hand, our spectroscopic data indicate that the specific differences in the effects of groups of the type of $NHCOCH_3$ and OCH_3 and of groups of the type of NH_2 and NMe_2 on the electronic charge at the meta C atom are in agreement with the estimates of electronic density on the basis of the magnetic parameter [13].

When the NH group is alkylated, we obtain for H, Me, Et, C_3H_7, and iso-C_3H_7 Δλ = 0, - 8, -3, -4, -5 mμ, respectively (Table 1, Nos. 1, 7, 12, 17, and 22). Such a strong hypsochromic effect of CH_3 (1, 7) is explained by disruption of the coplanarity of rings a and b and by the removal of the N atom of the NRΦ group from conjugation with ring a (as has been observed for NMe_2 [14]). The effect of other alkyl groups was similar, but it varied depending on competing inductive and steric effects. When p'-A^2 was introduced into p-$O_2N\Phi N(Me)\Phi$, there was a bathochromic effect: for p-A^2 = H, OCH_3, $NHCOCH_3$, NH_2, NMe_2 Δλ = 0, + 1, + 4, + 10, + 10 mμ, respectively (Table 1, Nos. 7-11). This confirms the hypothesis that here, as in the case of (III), there is only

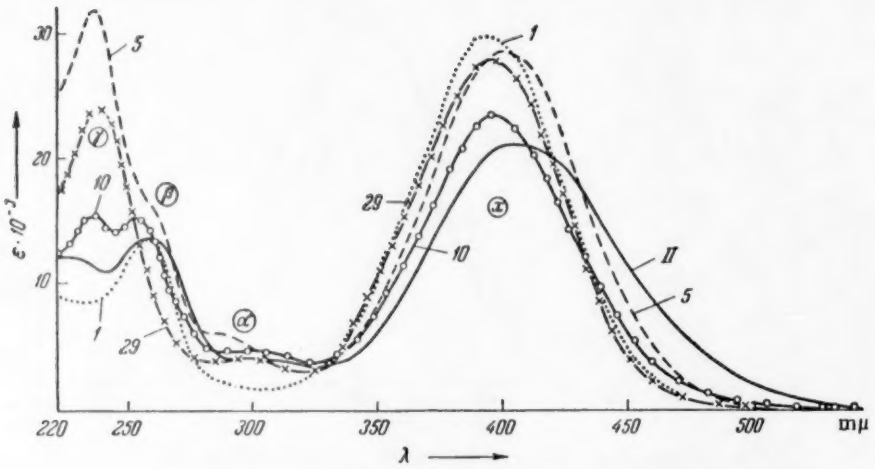


Fig. 2, 1, 5, 10, and 29) see Table 1; II) p-$O_2N\Phi NH\Phi NH_2$-p'.

inductive interaction of BKA and A^2K. When we compare λ_{max} for Nos. 8-11 with λ_{max} for the parent compound, No. 1, the effect of p-OCH_3 and of p-$NHCOCH_3$ is clearly hypsochromic, $\Delta\lambda$ = - 4, - 4 mμ, and only for p-NH_2 and p-NMe_2 does $\Delta\lambda$ = + 2, + 2 mμ. The bathochromic effect ($\Delta\lambda$ = + 3, + 3, + 7, and + 7 mμ) observed in place of a hypsochromic effect when m-A^2 = OCH_3, $NHCOCH_3$, NH_2, and NMe_2 was introduced into No. 7 was unexpected; the origin of this effect requires clarification. However, the simultaneous introduction of m-A^2 and CH_3 gave, upon comparison with the parent compound, No. 1, a hypsochromic effect: for m-OCH_3 and m-$NHCOCH_3$ $\Delta\lambda$ = - 5, -5 mμ; for m-NH_2 and m-NMe_2, $\Delta\lambda$ = 0 and 0 mμ (Table 1, Nos. 1 and 27-30).

Compounds Nos. 2-30 have been described previously [15].

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•Original Russian pagination. See C. B. translation.

ORGANOMAGNESIUM COMPOUNDS OF THE ISOXAZOLE SERIES

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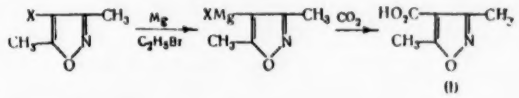
Although organomagnesium compounds of a number of nitrogen-containing heterocycles (pyridine, thiazole, pyrazole) have been prepared in recent years [1, 2], such compounds in the isoxazole series are still unknown. The reason for this is undoubtedly associated with the reactivity of the isoxazole ring with respect to highly active nucleophilic reagents.

We have now been able for the first time to prepare organomagnesium compounds of 3,5-dimethylisoxazole, and to show that they behave normally in Grignard reactions. As in other cases of nitrogen heterocycles [1, 2], isoxazolylmagnesium halides were obtained by the interaction of 3,5-dimethyl-4-bromo- and 3,5-dimethyl-4-iodoisoxazole with magnesium under reaction conditions which included the presence of ethyl bromide as an "entrainer" and solvents ordinarily used in the synthesis of organomagnesium compounds. The reaction was studied under various conditions, the yields being determined from the yield of 3,5-dimethylisoxazole-4-carboxylic acid (I), which was prepared by carboxylation of the Grignard compound. This acid was shown to be identical with a known sample [3]:

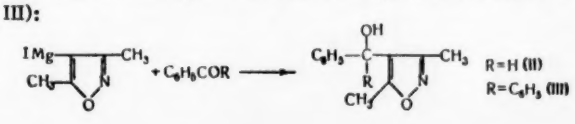


(I)

The experimental results are presented in the table.

The data indicate that the use of the iodide gives significantly better results than does the use of the bromide, and the yield of isoxazolylmagnesium halide depends on the amount of ethyl bromide used as an "entrainer." The most satisfactory results are obtained through the use of a twofold excess of the latter, because as was shown experimentally, a further increase in the amount of ethyl bromide does not increase the yield, and it makes separation of the isoxazolecarboxylic acid more difficult. Substitution of tetrahydrofuran for the diethyl ether increases the yield only insignificantly, although it is possible to use only one equivalent of ethyl bromide; we were unable to prepare the organomagnesium compound in dibutyl ether owing to tar formation in the reaction mixture. The most satisfactory method for preparative purposes involves interaction of the isoxazole halide and magnesium in ether in the presence of two equivalents of ethyl bromide, and this method was used in our further work.

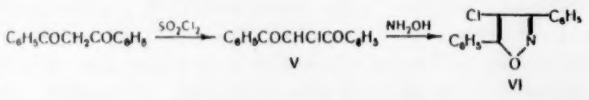
The isoxazolylmagnesium halides prepared in the present work can be used in typical Grignard syntheses. Thus, we carried out reactions with benzaldehyde and with benzophenone, which led to the corresponding arylisoxazolylcarbinols (II and III):



Preparation of 3,5-Dimethylisoxazole-4-carboxylic Acid from 3,5-Dimethyl-4-haloisoxazoles

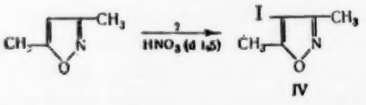
Expt. No.	X	No. equivs. C_2H_5Br/equiv. haloisoxazole	Solvent	Yield of acid, %
1	Br	1	Diethyl ether	15
2	Br	2	" "	32
3	Br	2	Dibutyl ether	—
4	I	1	Diethyl ether	36
5	I	2	" "	53
6	I	1	Tetrahydrofuran	56
7	I	2	"	57

These results show that organomagnesium compounds of the isoxazole series have rather high reactivity, exceeding, in particular, the activity of the corresponding pyridine derivatives [1]. As indicated above, 3,5-dimethyl-4-iodoisoxazole forms the organomagnesium derivative in higher yield than does the corresponding bromide. However, there is presently no convenient method for the synthesis of iodoisoxazoles; therefore, in connection with our investigation of isoxazolylmagnesium halides, we developed a special method for the preparation of 3,5-dimethyl-4-iodoisoxazole (IV) by direct iodination of 3,5-dimethylisoxazole—by the action of iodine in the presence of nitric acid; the yield is 85%.



This is a new substitution reaction for isoxazoles, and, in all probability, it is a general method for the synthesis of previously unknown isoxazoles; the method will be described in more detail in future communications.

Since the high sensitivity of the isoxazole ring to nucleophilic reagents and the effect of substituents on the extent of this sensitivity are well known, it would be expected that the ability of isoxazoles to form organomagnesium compounds would be rather specifically limited. This found partial confirmation in our attempt to prepare the organomagnesium derivative of diphenylisoxazole. 3,5-Diphenyl-4-chloroisoxazole (VI) was synthesized by the following scheme:



Dibenzoylmethane was chlorinated with sulfuryl chloride, and the resulting chloride, which was obtained in 86% yield, was cyclized by the action of hydroxylamine to chloroisoxazole VI.

It should be remarked that we were unable to accomplish the analogous cyclization of dibenzoyliodomethane, since the hydroxylamine reduced the iodide to the original dibenzoylmethane (cf. [4]).

When chloride VI was reacted with magnesium under our optimum conditions, dibenzoylchloromethane was the sole reaction product isolated, and it proved to be identical with the original sample. The mechanism of the opening of the isoxazole ring under these conditions is still not clear; we are presently continuing our investigation of Grignard reactions and closely similar reactions in the isoxazole series.

EXPERIMENTAL

3,5-Dimethyl-4-iodoisoxazole (IV). A solution of 37.3 g (0.147 mole) of iodine in 31.3 g (0.322 mole) of 3,5-dimethylisoxazole was heated on a water bath, and to it was added dropwise, with vigorous stirring, 13.6 ml (20.4 g, 0.324 mole) of nitric acid (d 1.5). Upon completion of the addition, the reaction mixture was heated for 30 min on a boiling water bath (the color was destroyed during the heating). The reaction mixture was cooled, and the precipitated crystals were filtered off, washed on the filter (from traces of nitroisoxazole) with 10% NaOH and with water, and dried. The yield was 55.4 g (85%); m.p. 51.5-53° (literature value [5], 52.5-54°.)

Found %: C 27.00; 26.77; H 2.95; 3.01

C_5H_6INO. Calculated %: C 26.94 H 2.71

3,5-Dimethylisoxazole-4-carboxylic acid (I). To 2.7 g (0.112 g atoms) of magnesium under a layer of 20 ml of ether was added dropwise, with vigorous stirring, 1.5 g of ethyl bromide (i.e., 1.5 g out of a total amount of 8.15 g—0.075 mole) and then a solution of 8.3 g (0.037 mole) of IV and the remainder of the ethyl bromide in 25 ml of ether. The addition was carried out at such a rate that the ether boiled smoothly. The mixture was then refluxed for an hour and cooled, and the solid carbon dioxide was added. The mixture was then made acid with hydrochloric acid (1 : 1). The ether layer and the ether extracts of the aqueous layer were agitated several minutes with 10% NaOH in a separatory funnel. The alkaline layer was separated and neutralized with hydrochloric acid (1 : 1), and the precipitated acid was filtered and dried. The yield was 2.77 g (53%); m.p. 141.5-142°. A mixture with a known sample [3] showed no depression of the melting point. The results of experiments under other conditions are shown in the table.

3,5-Dimethyl-4-isoxazolylphenylcarbinol (II). A solution of the organomagnesium compound, prepared as described above from 11.15 g (0.05 mole) of IV, 10.9 g (0.1 mole) of ethyl bromide, and 3.6 g (0.15 g atom) of magnesium in 70 ml of ether, was cooled to 0°, and a solution of 9.25 g (0.087 mole) of benzaldehyde in 20 ml of ether was added dropwise with vigorous stirring. The mixture was refluxed for 2 hr, cooled, and decomposed with hydrochloric acid (1 : 1). The ether layer was separated and dried over magnesium sulfate. The solvent was removed by distillation, and the residue was distilled under vacuum to yield 2.6 g of 3,5-dimethylisoxazole and 1.0 g of II, which boiled at 145-152°/3 mm. A second distillation gave 0.8 g of II (17%, based on the isoxazole reacted); b.p. 150-152°/3mm; m.p. 52.5-53.5° (from a mixture of ether and n-pentane.)

Found %: C 71.41; 71.27; H 6.46; 6.83; N 7.13; 7.17

$C_{12}H_{13}NO_2$. Calculated %: C 70.92 H 6.45; N 6.89

3,5-Dimethyl-4-isoxazolyldiphenylcarbinol (III). A solution of the organomagnesium compound, prepared in a manner similar to that described above from 11.15 g of IV, 10.9 g of ethyl bromide, and 3.6 g of magnesium in 50 ml of ether, was cooled to 0°, and a solution of 27.3 g (0.15 mole) of benzophenone in 40 ml of ether was added dropwise with stirring. After refluxing for two hours, the mixture was decomposed with hydrochloric acid (1 : 1); the precipitate (3.4 g) was filtered off, and the ether layer was separated and dried over magnesium sulfate. After distillation of the solvent, the residue was subjected to fractional crystallization from aqueous methanol, and an additional 2.6 g of III was thereby obtained. The over-all yield was 6 g (43%); m.p. 140-141° (from aqueous methanol.)

Found %: C 77.17; 77.31; H 6.24; 6.25

$C_{18}H_{17}NO_2$. Calculated %: C 77.41 H 6.14

Dibenzoylchloromethane (V). To a solution of 14.4 g (0.064 mole) of dibenzoylmethane in 100 ml of glacial acetic acid was added dropwise, with stirring, 8.67 g (0.064 mole) of sulfuryl chloride. The reaction mixture was heated for 2.5 hr at 50°, cooled, and highly diluted with water. The resulting precipitate was filtered and dried. The yield of V was 14.33 g (86%); m.p. 87-88° (literature value, 87-88° [6]).

3,5-Diphenyl-4-chloroisoxazole (VI). A solution of 9.16 g (0.035 mole) of V and 2.75 g (0.04 mole) of hydroxylamine hydrochloride in 50 ml of methanol was refluxed 5 hr and then cooled. The resulting precipitate was filtered off, and the filtrate was evaporated. The yield was 8.2 g (91%) of VI; m.p. 84° (from methanol.)

Found %: C 70.07; 69.92; H 4.23; 4.23; N 5.50; 5.33

$C_{15}H_{10}ClNO$. Calculated %: C 70.46 H 3.94 N 5.48

Interaction of VI with magnesium in the presence of ethyl bromide. To. 0.72 g (0.03 g atom) of magnesium covered by 15 ml of ether was added dropwise a solution of 2.55 g (0.01 mole) of VI and 2.2 g (0.02 mole) of ethyl bromide in 30 ml of ether, and the mixture was refluxed for 5 hr. The mixture was treated in the manner described for the preparation of 2,5-dimethylisoxazole-4-carboxylic acid, and 1 g of dibenzoylchloromethane was obtained; m.p. 86-87°. A mixture with a known sample showed no depression of the melting point.

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NITRATION OF TRIPHENYLOXONIUM AND DIPHENYLHALONIUM SALTS

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The present work included the study of diphenylchloronium, diphenylbromonium, and triphenyloxonium salts (specifically, the fluoborates), which we have previously prepared and described [1]. When both of these diphenylhalonium salts were nitrated with a strong nitration mixture, the nitro group almost exclusively entered the meta position, both at room temperature and at 100°, forming the di-m-nitrodiphenylhalonium salt in good yield. Meta orientation in both of these cases was more sharply expressed than in the case of diphenyliodonium fluoborate (72% meta and 28% para). The reaction rate decreases in the series:

$$(C_6H_5)_2I^+ > (C_6H_5)_2Br^+ > (C_6H_5)_2Cl^+.$$

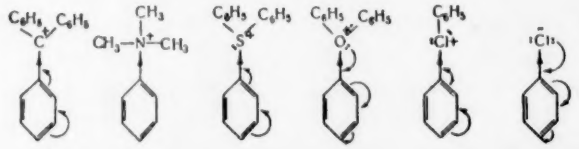
Condequently, orientation during nitration of diphenylhalonium salts obeys, in principle, the general rules for nitration of aromatic onium salts – meta orientation. Indeed, nitration of phenyltrimethylammonium [2], phenyltrimethylphosphonium [3], phenyldimethylsulfonium, and phenyldimethylselenonium [4] salts takes place solely in the meta position. Nitration of phenyltrimethylarsonium salts [3] gives 98% of the meta isomer, nitration of phenyltrimethylstibonium salts [3] gives 86%, and nitration of diphenyliodonium salts [5] gives 80% of the meta isomer.

Nitration of triphenyloxonium fluoborate does not take place at room temperature, even with strong nitration mixture (1 part of NHO_3, d = 1.52 and 1.5 parts of H_2SO_4, d = 1.84.) This substance, which is extremely inert in electrophilic substitution reactions, can be nitrated with this mixture only by heating to 100° over a period of 60 hr. This procedure yields almost pure tri-p-nitrotriphenyloxonium fluoborate in a yield of 80% of theoretical. Thus, the triphenyloxonium cation is a remarkable exception among all of the known phenyl onium cations. Suspecting the possibility of a free radical mechanism (owing to NO_2 and nitrogen oxides) under such vigorous conditions, we carried out nitration of triphenylsulfonium, phenyltrimethylammonium, and diphenylbromonium fluoborates under precisely the same conditions. Under these conditions, these onium salts nitrated almost completely in the meta position. On the other hand, nitration of triphenyloxonium fluoborate by means of NO_2BF_4, which proceeds even at room temperature, gives a 92% yield of the same tri-p-nitrophenyloxonium fluoborate.

Thus, para orientation during electrophilic substitution in the triphenyloxonium cation—which is an exceptional case among the onium compounds—is an experimental fact. It is not very probable that the peculiar behavior of the triphenyloxonium cation can be explained by steric factors. The comparison with the triphenylcarbonium cation, which nitrates exclusively in the meta position [6], is persuasive on this point. $(C_6H_5)_3C^+$ has a spirally distorted planar form. The trigonally pyramidal form (the presence of a free pair of electrons) of the triphenyloxonium ion distinguishes it from the triphenylcarbonium ion. In this case, there should be rotation of the planes of the phenyl groups about the C-O axis relative to the faces of the trigonal pyramid, and this should be more highly developed than the spiral rotation of the phenyls of $(C_6H_5)_3C^+$. On the one hand, such

rotation should decrease steric hindrance [and in $(C_6H_5)_3C^+$, this hindrance does not affect attack on the meta position], and, on the other hand, it must to some extent remove the free pair of electrons from conjugation (removal must be complete when the rotation is 90°). Both factors would favor meta orientation.

Apparently, the sole conceivable reason for the unusual behavior of the triphenyloxonium ion during nitration is the same reason which underlies ortho–para orientation during electrophilic substitution in halobenzenes, with the exception of fluorobenzene. It is interesting to compare orientation during electrophilic substitution in the series of phenyl onium cations, both among themselves and with the triphenylcarbonium cation and halobenzenes.



It is evident that the triphenyloxonium cation has one property in common with all of the substances enumerated—an orientational inductive effect of the key atoms. In contrast to the carbonium and ammonium ions and like the sulfonium and halonium ions, the key (oxygen) atom of the oxonium ion has a free pair of electrons. Like the nitrogen of ammonium and in contrast to sulfur and the halogens, expansion of the octet of the oxygen atom in oxonium salts is impossible. All of this provides us with grounds for the following explanation: The very strong negative inductive effect of the oxonium oxygen, which highly passivates the phenyls, nevertheless, as in the halobenzenes, is overshadowed by conjugation of the free pair of electrons of the oxygen atom with the pi electrons of the phenyls (+ T effect). In the halonium ions, the electron pairs are not so inert, and behave normally only in diphenyliodonium salts (20% yield of the paranitro compound). In the triphenyl sulfonium ion, the only conceivable conjugation of the electron pair of the sulfur (+ tautomeric effect) is overshadowed by the (-) tautomeric effect due to the possible entry of the pi pair of the phenyl in the shell of the sulfur as a consequence of expansion of the octet, which is possible in this case. This possibility also applies to the halogen of halonium ions, but not to the nitrogen of ammonium ions. However, there is no free pair at the nitrogen of ammonium ions which could cause a + T effect. The result is pure meta orientation owing to the –I effect of the nitrogen atom. Finally, in the triphenylcarbonium cation we have a case of pure meta orientation owing to the congruent –I and –T effects.

EXPERIMENTAL

The experimental conditions and the results of the experiments on the nitration of onium fluoborates are presented in Table 1. The position of the nitro group in the nitration products was determined by decomposition of the latter with pyridine, aqueous NaOH and $(CH_3)_2NH$ solutions, or thermally. The analyses and decomposition temperatures of all of those trinitrotriphenyloxonium, trinitrotriphenylsulfonium, dinitrodiphenylbromonium, and dinitrodiphenylchloronium salts, which were obtained for the first time in the present work are shown in Table 2.

Alkaline decomposition of $[(NO_2C_6H_4)_3O]BF_4$. a) A mixture of 0.56 g of trinitrotriphenyloxonium fluoborate (Table 1, Expt. 1) and 15 ml of 20% NaOH solution was refluxed for 2.5 hr. The usual treatment gave 0.4 g (91% of theoretical) of dinitrodiphenyl ether with an m.p. of 141.5-143° (reference [8] gives an m.p. of 142-143° for p,p'-dinitrodiphenyl ether) and a mixture of isomeric nitrophenols, which, according to paper chromatography [9], contained absolutely no meta isomer. b) Similar treatment of 0.3 g of trinitrotriphenyloxonium fluoborate, prepared in Expt. 2 (and also in Expt. 3), gave 0.16 g of a dinitrodiphenyl ether with an m.p. of 122-134°, which, judging from its u.v. spectrum, was a mixture of 95% p,p'-dinitrodiphenyl ether and 5% of the o,o'-isomer. The paper chromatograms of the nitrophenols separated from the reaction mixture showed no spot corresponding to m-nitrophenol.

Decomposition of $[(NO_2C_6H_4)_3O]BF_4$ with dimethylamine. A mixture of 0.65 g of trinitrotriphenyloxonium fluoborate (Table 1, Expt. 1) and 10 ml of a 45% aqueous solution of $(CH_3)_2NH$ was allowed to stand for a day at room temperature. The usual treatment gave 0.34 g (94% of theoretical) of dinitrodiphenyl ether with an m.p. of 139-141° and 0.07 g (31% of theoretical) of nitrodimethylaniline, m.p. 160.5-162° (reference [10] gives an m.p. of 161-162° for p-nitrodimethylaniline.)

TABLE 1

Expt. No.	Original salt, g	Reagents,[1] ml	Reaction conditions	Reaction product: formula	decomp. temp., °C	Yield, %	isomer ratio: meta, %	isomer ratio: para and ortho, %
1	$[(C_6H_5)_3O]BF_4$ 1	HNO_3 8,5 H_2SO_4 13,3	Sealed tube, 100°, 60 hr	$[(NO_2C_6H_4)_3O]NO_3$ 0,25 g $[(NO_2C_6H_4)_3O]BF_4$ 0,83 g	126—127 216—217	80[2]	Non-separated	Almost 100% para
2	The same 0,33	NO_2BF_4,[3] 0,85 g CH_3NO_2 5	Stirred at room temp., 70 hr	$[(NO_2C_6H_4)_3O]BF_4$ 0,43 g		92[4]	Same	95% para, 5% ortho
3	The same 0,25	NO_2BF_4 1,0 g CH_3NO_2 5	Sealed tube, 100°, 23 hrs	$[(NO_2C_6H_4)_3O]BF_4$ 0,28 g	185—195	74[4]	Same	The same
4	$[(C_6H_5)_3S]BF_4$ 1,47	HNO_3 11,3 H_2SO_4 19,0	Same, 60 hr	$[(NO_2C_6H_4)_3S]BF_4$ 1,42 g	224—225	70[5]	~ 100	None separated
5	$[C_6H_5N(CH_3)_3]BF_4$ 1,65	HNO_3 7,0 H_2SO_4 11,0	The same	$[NO_2C_6H_4N(CH_3)_3]I$ 2,0 g	185—187	88[6]	96	4 para
6	$[(C_6H_5)_2Br]BF_4$ 1,5	HNO_3 12,0 H_2SO_4 21,0	The same	$[(NO_2C_6H_4)_2Br]NO_3$ 0,52 g $[(NO_2C_6H_4)_2Br]Br$ 1,17 g	109—110 95—95,5	91[5]	94	6 para
7	The same 3,1	HNO_3 5,0 H_2SO_4 12,0	18—20°, 94 hr	$[(NO_2C_6H_4)_2Br]Br$ 3,6 g	94—95	92[5]	~ 100	None separated
8	$[(C_6H_5)_2Cl]BF_4$ 2,5	HNO_3 4,5 H_2SO_4 11,5	The same, 720 hr	$[(NO_2C_6H_4)_2Cl]_2PtCl_6$ 2,33 g	147—148	49[5]	~ 100	None separated

[1]In all experiments: HNO_3 (d 1.52), H_2SO_4 (d 1.84). [2]The reaction mixture was poured onto ice, neutralized with soda, and, after removal of the precipitated nitrate, treated with a saturated solution of $NaBF_4$ or NaBr (Expt. 6.) [3]Prepared by the method of reference [7]. [4]The reaction mixture was filtered from excess NO_2BF_4 and diluted with absolute ether. [5]The reaction mixture was poured onto ice and treated with a concentrated solution of $NaBF_4$, NaBr (Expt. 7), or H_2PtCl_6 (Expt. 8) without preliminary neutralization of the excess acid. [6]The reaction mixture was poured onto ice, neutralized with soda, and treated with a concentrated solution of NaI.

Decomposition of $[(NO_2C_6H_4)_3O]BF_4$ with pyridine. A mixture of 0.7 g of trinitrotriphenyloxonium fluoborate, prepared in Expt. 1, and 5.5 ml of pyridine was refluxed 24 hr. The excess pyridine was removed, and 0.33 g (85% of theoretical) of p,p'-dinitrodiphenyl ether, m.p. 141-142°, was obtained.

Alkaline decomposition of $[(NO_2C_6H_4)_3S]BF_4$. A mixture of 1.36 g of trinitrotriphenylsulfonium fluoborate and 15 ml of a 10% solution of NaOH was refluxed for 25 hr. There was obtained 0.58 g (75% of theoretical) of crude m,m'-dinitrodiphenyl sulfide, which was identified by oxidation with CrO_3 in glacial acetic acid to the sulfone with an m.p. of 193-197° (reference [11] gives an m.p. of 197° for m,m'-dinitrodiphenyl sulfone) and a mixture of nitrophenols which, according to paper chromatography, was a mixture of m-nitrophenol and p-nitrophenol.

Decomposition of $[(NO_2C_6H_4)_3S]BF_4$ with pyridine. A mixture of 0.56 g of trinitrotriphenylsulfonium fluoborate and 3 ml of pyridine was heated in a sealed tube to 225° over a period of 3 hr and then for an additional 15 min at this temperature. The excess pyridine was removed, and 0.23 g (72% of theoretical) of m,m'-dinitrodiphenyl sulfide, m.p. 104.5-106.5°, was obtained; this was identified by oxidation to the sulfone with an m.p. of 197-199°.

Thermal decomposition of $[NO_2C_6H_4N(CH_3)_3]I$. A sample of 1.5 g of nitrophenyltrimethylammonium iodide was decomposed by heating under vacuum to 200°/5mm. There was obtained 0.8 g (99% of theoretical) of a mixture of isomeric nitrodimethylanilines, from which steam distillation separated 0.74 grams of

TABLE 2

Expt. No.	Salt	Decomp. temp., °C	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
1	$[(p\text{-}NO_2C_6H_4)_3O]BF_4$	216–217	46,06 46,19	46,09	2,56 2,66	2,58	8,96 8,93	8,95
2	$[(p\text{-}NO_2C_6H_4)_3O]HgI_3$	159–160	22,68 22,53	22,44	1,44 1,40	1,26		
3	$[(p\text{-}NO_2C_6H_4)_3O]NO_3$	126–127	48,44 48,58	48,67	2,84 2,94	2,79	12,82	12,60
4	$[(p\text{-}NO_2C_6H_4)_3O]C_6H_3(NO_2)_3O$	158–159	47,24 47,07	47,23	2,16 2,15	2,31	14,24	13,73
5	$[(p\text{-}NO_2C_6H_4)_3O]_2PtCl_6$	182–183	36,85 36,70	36,87	2,30 2,31	2,06		
6	$[(p\text{-}NO_2C_6H_4)_3O]B(C_6H_5)_4$	158–159	71,91 71,66	71,90	4,95 4,65	4,60	5,83 5,88	5,97
7	$[(m\text{-}NO_2C_6H_4)_2S]BF_4$	224–225	44,67 44,47	44,56	2,39 2,40	2,49	8,59 8,74	8,66
8	$[(m\text{-}NO_2C_6H_4)_2S]I$	194–195	41,35 41,38	41,17	2,39 2,34	2,30	8,18 8,12	8,00
9	$[(m\text{-}NO_2C_6H_4)_2Br]NO_3$	116–117	37,39 37,58	37,33	2,29 2,23	2,10	11,07 10,88	10,88
10	$[(m\text{-}NO_2C_6H_4)_2Br]Br$	94–95	35,43 35,42	35,67	1,98 1,96	2,00	6,68 6,61	6,93
11	$[(m\text{-}NO_2C_6H_4)_2Br]Cl$	98–100	40,00 40,02	40,07	2,43 2,43	2,25	8,06 7,84	7,79
12	$[(m\text{-}NO_2C_6H_4)_2Cl]HgBr_3$	123–124,5	20,30	20,02	1,20	1,12	3,98	3,89
13	$[(m\text{-}NO_2C_6H_4)_2Cl]_2PtCl_6$	147–148	29,64	29,80	1,90	1,67	6,02	5,79

Note: All of the salts shown in Table 2, with the exception of the 3rd, 9th, and 11th, were difficultly soluble in cold water; the majority were readily soluble in acetone, lower alcohols, and nitromethane; all of the salts were insoluble in ether and hydrocarbons.

m-nitrodimethylaniline with an m.p. of 58.5-60.5° (reference [12] gives an m.p. of 59-60° for m-nitrodimethylaniline) and 0.03 g of impure p-nitrodiphenylaniline with an m.p. of 110-120°.

Thermal decomposition of $[(NO_2C_6H_4)_2Br]Br$. a) Thermal decomposition of 0.5 g of dinitrodiphenylbromonium bromide, prepared in Expt. 7, gave 0.42 g (84% of theoretical) of bromonitrobenzene with an m.p. of 54.5-55.5°. A mixture of this with known m-nitrobromobenzene melted without depression of the melting point. b) When 0.42 g of the dinitrodiphenylbromonium bromide prepared in Expt. 6 was decomposed under the same conditions, 0.4 g (95% of theoretical) of bromonitrobenzene with an m.p. of 46-49° was formed. The ultraviolet spectrum of this substance showed it to be a mixture of 94% of the meta and 6% of the para isomer.

Alkaline decomposition of $[(NO_2C_6H_4)_2Cl]_2PtCl_6$. A mixture of 0.46 g of dinitrodiphenylchloronium chloroplatinate and 15 ml of a 20% solution of NaOH was allowed to stand at room temperature for three days. According to its paper chromatogram, the resulting mixture of nitrophenols was composed mainly of m-nitrophenol with a trace of p-nitrophenol.

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ISOMERIZATION OF THE n-PROPYL CARBONIUM ION

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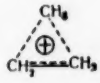
Roberts and Halmann [1] have described the rearrangement of the n-propyl carbonium ion;

$$CH_3-CH_2-C^{14}H_2^+ \rightleftarrows {}^+CH_2-C^{14}H_2-CH_3;$$

during the reaction of C^{14}-labeled n-propylamine with nitrous acid:

$$CH_3-CH_2-C^{14}H_2-NH_2 \xrightarrow{HNO_2} CH_3-C^{14}H_2-CH_2-OH\ .$$

It is natural that this interesting rearrangement has attracted the attention of chemists, since it represents the simplest case of pinacolone-type rearrangement. This rearrangement is already described in the newest organic chemistry textbooks; the concept of the simplest nonclassical cation has been introduced on the basis of this rearrangement:



We have recently shown [2] that the propyl free radical does not undergo skeletal rearrangement in carbon tetrachloride solution. Instead, isomerization occurs with migration of a hydrogen atom from the beta position:

$$CH_3-CH_2-C^{14}H_2\cdot \rightleftarrows \cdot CH_2-CH_2-C^{14}H_3.$$

With the rather frequently observed analogy in the behavior of radicals and cations in mind, we analyzed the above work of Roberts and Halmann [1], and we have found that their conclusion as to the character of the rearrangement of the propyl carbonium ion is not the only one possible.

The authors concluded that the C^{14} carbon occupies the second position in the resulting molecule of n-propyl alcohol ($CH_3-C^{14}H_2-CH_2-OH$); this conclusion was reached on the basis of the activity of the ethylamine formed as a result of the following reaction:

$$CH_3-CH_2-C^{14}H_2-NH_2 \xrightarrow{HNO_2} CH_3-CH_2-CH_2-OH \xrightarrow{KMnO_4}$$
$$\rightarrow CH_3-CH_2-COOH \xrightarrow{HN_3} \underset{\text{active}}{CH_3-CH_2-NH_2} + CO_2.$$

That the radioactive C^{14} carbon was joined directly to the nitrogen in the ethylamine molecule was assumed by the authors without experimental proof.

If the C^{14} is actually in the methyl group of the ethylamine molecule, the propyl carbonium ion did not undergo pinacolone-type rearrangement, but isomerized by migration of a hydride ion.•

•It should be noted that isomerization of the n-propyl carbonium ion to an isopropyl carbonium ion during the

We repeated the work of Roberts and Halmann, and established that these authors were in error.•

In actuality, under the conditions under consideration, the propyl carbonium ion undergoes isomerization similar to that which we discovered for the propyl radical, namely:

$$CH_3-CH_2-C^{14}H_2^+ \rightleftarrows {}^+CH_2-CH_2-C^{14}H_3.$$

The interaction of n-propylamine hydrochloride (activity 1.54 μC /millimole) with nitrous acid led to the formation of n-propyl and isopropyl alcohols.

$$CH_3-CH_2-C^{14}H_2-NH_2\cdot HClO_4 \xrightarrow{HNO_2} CH_3-CH_2-CH_2-OH + \\ + CH_3-CH(OH)-CH_3$$

Oxidation of the n-propyl alcohol with potassium permanganate gave propionic acid (activity, 0.57 μC per millimole), which was further oxidized with potassium dichromate to acetic acid (activity, 0.045 μC /millimole) and carbon dioxide.

$$CH_3-CH_2-CH_2-OH \xrightarrow{KMnO_4} CH_3-CH_2-COOH \xrightarrow{K_2Cr_2O_7} CH_3-COOH + CO_2$$

The acetic acid was: a) cleaved by the method of Schmidt,and b),in the form of the sodium salt, fused with a base.

In the first case, all of the activity of the acetic acid was transferred to the methylamine; in the second case, it was transferred to the methane:

$$CH_3-COOH \begin{cases} \xrightarrow{HN_3} C^{14}H_3-NH_2 + CO_2 + N_2. \\ \xrightarrow{NaOH} C^{14}H_4 + Na_2CO_3. \end{cases}$$

It is therefore clear that the n-propyl alcohol formed during the reaction of n-propylamine-1-C^{14} with nitrous acid contained radioactive C^{14} carbon only in the 1 and 3 positions.

By a similar route, we showed that the isopropyl alcohol also contained C^{14} in the 1 and 3 positions (but not in the 2 position).

This isomerization of the n-propyl carbonium ion (which we discovered) is either a single-stage process of migration of a hydride ion from the beta position

$$CH_3-CH_2-C^{14}H_2^+ \rightleftarrows {}^+CH_2-CH_2-C^{14}H_3 \qquad (I)$$

or a two-stage process of migration of a hydride ion from the alpha position:

$$\text{a) } CH_3-CH_2-C^{14}H_2^+ \rightleftarrows CH_3-\overset{+}{C}H-C^{14}H_3$$

$$\text{b) } CH_3-\overset{+}{C}H-C^{14}H_3 \rightleftarrows {}^+CH_2-CH_2-C^{14}H_3. \qquad (II)$$

The second mechanism is supported both by the fact that isopropyl alcohol was formed in the reaction and by the results of the study of hydrogen exchange in paraffins (for example, [5]). On the other hand, only the formation of isopropyl alcohol (without traces of n-propyl alcohol) by the action of nitrous acid on isopropylamine•• is described in the literature [6].

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reaction of n-propyl amine with nitrous acid was established some time ago [3]; among the products of this reaction was observed a significant amount of isopropyl alcohol (the yield of n-propyl alcohol was 7%; that of isopropyl alcohol was 32%).

•It should be pointed out that in work with other amines (3-aryl-1-propylamine-1-C^{14}), Roberts and co-workers [4] unconditionally demonstrated skeletal rearrangement during the reaction with nitrous acid.

••The results of this work require confirmation. Since the formation of n-propyl alcohol requires isomerization of the more stable isopropyl carbonium ion to the less stable n-propyl carbonium ion ($CH_3-\overset{+}{C}H-CH_3 \rightarrow \overset{+}{C}H_2-CH_2-CH_3$), it is evident that if this isomerization does take place, it does so only to a slight extent, and only a few percent n-propyl alcohol can be present in the reaction mixture.

Thus, the question of whether our isomerization occurs in one or two stages still remains open.

The ability to undergo isomerization by migration of hydride ions is undoubtedly a common property of alkyl carbonium ions, at least to some degree. Roberts and co-workers [7], for example, demonstrated such an isomerization for the ethyl carbonium ion during the reaction of ethylamine with nitrous acid. It is quite probable that such isomerization also occurs during conversions of alicyclic compounds by the Dem'yanov reaction.

For example, from this assumption, the conclusion follows that in cyclohexanol molecules resulting from the action of nitrous acid on cyclohexylamine, the hydroxyl group is connected not just to the carbon atom to which the amino group was connected in the original cyclohexylamine molecule.

Finally, it should be remarked that the absence of skeletal rearrangement of the propyl carbonium ion in the reaction studied in this work does not constitute proof, in any degree, that the rearrangement cannot proceed under other conditions.

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ADSORPTION OF HYDROGEN ON LOW PERCENTAGE Pt/Al_2O_3 AND Pd/Al_2O_3 CATALYSTS IN THE LIQUID PHASE

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In a study of hydrogenation catalysts, it is very important to know the quantity and condition of hydrogen sorbed by them. The literature throws ample light on this question, but most of the investigations deal with pure metals, mixed catalysts, or isolated examples of catalysts with relatively high percentages of an active metal deposited on them.

We prepared a series of Pt/Al_2O_3 and Pd/Al_2O_3 catalysts which contained 0.05 to 3.47% of the metal by weight.

Alumina gel, used as the carrier, was prepared by precipitating aluminum hydroxide from $Al_2(SO_4)_3$ with ammonia [1]. Samples for platinum and palladium were prepared separately, and consequently their specific surfaces may have differed slightly. To deposit the platinum and palladium on the Al_2O_3 powder, the latter was well shaken up with dilute solutions of $PtCl_4$ and $PdCl_2 \cdot 2NaCl$, at different concentrations, at room temperature. The shaking was continued for two hours in the case of platinum, and three hours for palladium. Adsorption of platinum was complete at all concentrations. Palladium was detected in the filtrate when its concentration on the carrier reached 0.6%. However, palladium which is precipitated on Al_2O_3 is adsorbed irreversibly and cannot be detected in the washings. The filtrates were analyzed photocolorimetrically for Pd^{++}. The catalysts were washed free from Cl^-, dried, and reduced in a stream of electrolytic hydrogen as follows: two hours at 220-230° followed by a rapid increase to 355° and further reduction at 355-360° for two hours. The catalysts were brought into contact with air on cooling to room temperature and stored in glass-stoppered bottles.

Chemical dehydrogenation is a convenient method for determining the amount of hydrogen sorbed by the catalyst. Benzoquinone can be hydrogenated quantitatively to hydroquinone by hydrogen sorbed on nickel, platinum, and palladium catalysts [2]. All the hydroquinone formed can be determined in solution in the presence of an excess of quinone.

EXPERIMENTAL METHOD

A weighed sample of catalyst (0.5 to 1.0 g), which had been brought to constant weight at 115-120°, was placed in a known volume of a solvent and shaken in an atmosphere of hydrogen. When the catalysts had been saturated with hydrogen the shaking was stopped, and the hydrogen in the gas phase displaced with purified nitrogen. In this atmosphere of nitrogen, the quinone solution was introduced and the shaking resumed. At the end of the experiment the catalyst was filtered quickly by suction, and the filtrate immediately analyzed for hydroquinone.

Water-alcohol suspensions of the carrier and the prepared catalysts have slightly different pH's, and so the reaction was carried out in a buffer solution—CH_3COOH + NaOH (acid concn. 0.14 N), pH 5.2. The volume of the solution was 20-25 ml and the times taken to saturate the catalysts with H_2 were 30-40 min for Pt/Al_2O_3

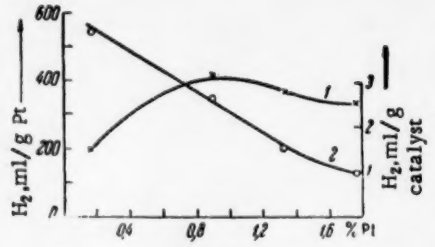

Fig. 1.

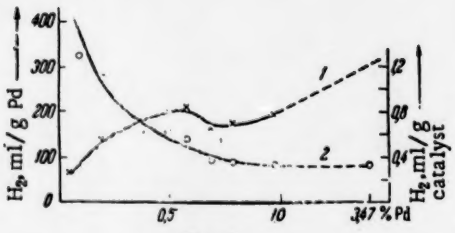

Fig. 2.

TABLE 1

Dehydrogenation of Pt/Al_2O_3 Catalysts by Quinone

Platinum content of catalyst, wt. %	Wt. of catalyst, g	Hydroquinone obtained, mg	Hydrogen taken up, ml		
			total	on 1 g catalyst	on 1 g Pt
0,171	0,498	2,51	0,511	1,03	600
0,171	0,756	3,21	0,650	0,86	505
0,893	0,472	7,34	1,49	3,16	354
1,331	0,449	6,59	1,34	2,98	224
1,331	0,504	6,43	1,31	2,59	195
1,766	0,490	6,04	1,26	2,51	142
1,766	0,452	6,48	1,32	2,56	145

and 40-50 min for Pd/Al_2O_3, depending on the palladium concentration. The reversible hydrogen potentials were $E_0(Pt)$ = 540-550 mv, $E_0(Pd)$ = 550-580 mv, relative to the normal calomel electrode. When 0.05 g of quinone (in 4 to 5 ml alcohol) was added, the potential of the catalysts decreased to the acid region at 720-730 mv. On shaking with the quinone (for 20-30 min in the case of Pt/Al_2O_3 and 40-60 min in the case of Pd/Al_2O_3), the potential increased by a few millivolts and then remained constant. The experiments were carried out at 25°. Blank experiments, without the catalysts, were carried out periodically. A small amount of hydroquinone was discovered in the solution and this was then taken into account.

Experiments with pure Al_2O_3 and also with mixtures of it and the catalysts showed that it did not adsorb hydrogen under the set conditions.

The hydroquinone was determined titrimetrically (using an ampere meter) with $Ce(SO_4)_2$ in 2N H_2SO_4 [3], and in addition the filtrate was analyzed iodometrically for quinone. Under the experimental conditions the amount of quinone adsorbed on the catalysts is within the analytical error. Experiments with larger weights of Al_2O_3 and quinone showed that less than 1 mg quinone was adsorbed by 1 g alumina.

Two to three parallel experiments were carried out on each catalyst, and with Pt/Al_2O_3 catalysts there was satisfactory reproducibility. Palladium catalysts gave more freakish results, the deviations in some cases reaching ± 20%. After an appropriate purification, the nitrogen was further passed through a series of bottles containing hydroquinone and pyrogallol absorbents, but it could not be completely freed from traces of oxygen, (detected by the decrease of potential in a standard experiment on a Ni grid); therefore, the results may be rather low.

The experimental results are shown in Tables 1 and 2; Figs. 1 and 2 contain the mean values from the parallel experiments. Curve 1 (Figs. 1 and 2) shows the relation between the volume (ml) of hydrogen taken up by 1 g catalysts (right-hand ordinate) and its composition. This quantity starts by increasing with increasing metal content and then decreases slightly. This transition occurs in the region 0.8-1% Pt for Pt/Al_2O_3, and 0.5-0.6% Pd for Pd/Al_2O_3. On further increasing the palladium content, the adsorption of hydrogen passes through a small minimum, and then increases again. The absolute amount of hydrogen adsorbed on Pd/Al_2O_3 is lower than on the analogous platinum compound. Larger amounts of hydrogen (about 3 ml per g catalyst) are adsorbed on the catalysts having the highest concentrations of metals studied: 1.766% Pt and 3.47% Pd (the latter appears at the limit of Fig. 2).

If the amount of hydrogen taken up is converted to the amount taken up by 1 g metal, it appears that the capacity to take up hydrogen increases as the portion of the catalyst surface taken up by the metals decreases (curve 2, Figs. 1 and 2).

TABLE 2

Dehydrogenation of Pd/Al_2O_3 by Quinone

Pd content of catalyst, wt.%	Wt. of catalyst, g	Hydroquinone obtained, mg	Hydrogen taken up, ml		
			total	on 1 g catalyst	on 1 g palladium
0,050	1,4360	1,64	0,33	0,23	460
0,050	1,0629	1,48	0,30	0,28	560
0,10	1,1652	1,57	0,33	0,27	274
0,10	1,0135	1,88	0,40	0,38	377
0,20	0,8554	1,87	0,39	0,44	223
0,20	0,7000	2,28	0,46	0,66	330
0,40	0,8556	2,52	0,51	0,60	149
0,40	0,5427	1,75	0,36	0,66	164
0,50	0,9848	4,54	0,92	0,94	186
0,50	0,6881	2,14	0,43	0,63	126
0,58	0,5177	2,49	0,51	0,98	168
0,58	0,5575	1,87	0,38	0,68	117
0,69	0,5445	1,84	0,37	0,68	99,4
0,69	0,7327	2,28	0,46	0,63	91,5
0,79	0,4990	1,54	0,31	0,63	79,5
0,79	0,5142	1,90	0,39	0,75	95,0
0,97	0,5310	1,97	0,40	0,76	77,8
0,97	0,5214	2,03	0,41	0,79	81,6
3,47	0,1982	3,00	0,61	3,09	89,1
3,47	0,1970	2,56	0,52	2,67	76,7

For a Pt content of 0.171%, 500 ml H_2 is taken up, i.e., about ten atoms of hydrogen to one atom of platinum, but for a content of 1.766% the ratio of Pt : H is less than three. Palladium behaves similarly: A catalyst with the lowest palladium concentration (0.05%) takes up most hydrogen (510 ml per g Pd or about five hydrogen atoms for each palladium atom). The palladium atom is approximately twice as small as a platinum atom, and its adsorption capacity for hydrogen is correspondingly smaller.

As their concentration is increased in the catalysts, the capacities of platinum and palladium to adsorb hydrogen fall sharply at first, and then more slowly. For Pt/Al_2O_3 the decrease in adsorption capacity becomes more gradual at 1.3-1.5% Pt content. Between 0.7 and 3.47% Pd the Pd : H ratio for Pd/Al_2O_3 is approximately unity. So even at a Pd content of 3.47% the amount of hydrogen adsorbed is not characteristic of the degree of dispersion of palladium on the catalyst surface. Under the conditions studied, the properties of low-metal-content Pt/Al_2O_3 and Pd/Al_2O_3 are in general very similar.

Specific properties of catalysts in very dilute layers on carriers have already been recorded. A. N. Mal'tsev and N. M. Kobozev [4] found that in hydrogenation of olefins on Pt/Al_2O_3 and Pt/SiO_2, the specific activity of platinum increased (at very low contents) with its decreasing surface coverage. It appeared that during this process there was also a large increase in the paramagnetic susceptibility of platinum. This excess paramagnetism was found for most samples of platinum, palladium and other catalysts in "super-diluted" layers [4]. These specific properties, shown by atoms of palladium and platinum when they are deposited in very small quantities on carriers of the type Al_2O_3 can, therefore, be considered as well established.

The explanation of this phenomenon must lie in the electronic interaction between the atoms deposited and the atoms of the carriers semiconductors). A single metal atom falling on the carrier surface builds up a field around itself, and so adsorbs hydrogen (apparently in the molecular form). Thus, the adsorbed catalyst atoms give rise to the well-known remote action effect. This representation agrees with the views of Patterson [6] on active centers in the wider field of surface diffusion. If the deposited platinum and palladium are assumed to exist in their crystalline forms, each surface metal atom should take up more hydrogen atoms than the number calculated.

The analogous behavior of platinum and palladium in dilute layers, with regard to adsorption of hydrogen in the liquid phase, confirms observations that the catalytic properties (for example, in the hydrogenation of compounds containing triple bonds) of palladium on a carrier are more like those of platinum than of pure palladium.

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A STUDY OF COMPLEX FORMATION BETWEEN CERTAIN α-HYDROXY ACIDS AND YTTRIUM AND CERIUM

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Complex formation between certain α-hydroxy acids and rare earth elements has been applied to the chromatographic separation of mixtures of these elements [1-3]. However, the literature contains no data from which may be determined the best structure and composition of the hydroxy acid. We have studied complex formation of yttrium and of cerium with aliphatic hydroxy acids having different numbers of carbon atoms—glycolic, lactic, α-hydroxyisobutyric, α-hydroxyisovaleric, and α-hydroxyisocaproic. Equimolar amounts of the radioisotopes of yttrium and cerium were used without a carrier. The glycolic and lactic acids were commercial products; the α-hydroxybutyric acid was synthesized by the method of reference [4], and the α-hydroxyisovaleric and α-hydroxyisocaproic acids were synthesized by the methods of references [5] and [6], respectively.

Cation-exchange resin KU-2 was used as the solid phase; it had a grain size of 0.25-0.50 mm and a DVB content of approximately 8%. The solutions used in the course of the work contained Y^{91} or Ce^{144}, and had a specific activity of about 6000 impulses per minute. The activity was measured with an end-window counter.

The study of the distribution coefficients of Y^{3+} and Ce^{3+} between the resin and the solution was carried out under static conditions. Radioactivity measurements were carried out on the original solution and on the solution remaining after equilibrium had been established with the resin. The cation-exchange resin was used in the Na form. The concentrations of the solutions of the complexing agents were varied from 10^{-3} to $2 \cdot 10^{-1}$ M. The concentration of the complexing anion was varied by neutralizing the original solution of the given acid (in constant concentration) with different amounts of NaOH. The concentration of anion participating in complex formation was determined as the sum of the concentration of neutralized acid and of anions formed by dissociation of the residual acid under the given conditions. The ionic strength was maintained constant ($\mu = 0.2$) by means of $NaClO_4$.

Several series of experiments were carried out with glycolic, lactic, α-hydroxyisobutyric, and α-hydroxyisovaleric acids and with Y^{91} and Ce^{144} separately; the over-all acid concentrations were 0.005, 0.05, and 0.2 M. The NaOH solutions had concentrations of 0.01, 0.1, and 0.4 N, respectively. Moreover, experiments were carried out with different over-all acid concentrations, but at constant pH. These experiments gave results similar to those obtained from the other experiments.

The distribution coefficients φ were calculated by means of the equation $\varphi = xv/cm$, where x is the fraction of the activity remaining with the resin, c is the fraction of the activity in the solution, v is the volume of the solution, and m is the weight of the air-dried resin in grams. In carrying out the experiments, a drop of the original solution of the radioactive element was evaporated to remove the mineral acid, and the residue was treated with the solution of organic acid having a concentration indicated above. Ten ml of the resulting solution was placed in a test tube specially designed for agitation; the ion-exchange resin was introduced, and

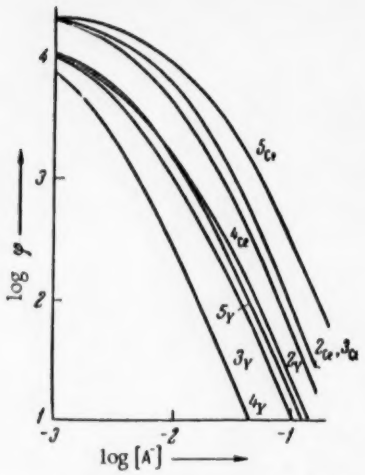

Fig. 1. Relationship between the distribution coefficient (φ) and concentration of the anion ligand ([A^-]). 2_Y) yttrium–glycolic acid system; 3_Y) yttrium–lactic acid system; 4_Y) yttrium–hydroxyisobutyric acid system; 5_Y) yttrium–hydroxyisovaleric acid system; ^2Ce, ^3Ce, ^4Ce, and ^5Ce – same for systems containing cerium ions.

predetermined amounts of NaOH, $NaClO_4$, and water were added to bring the total volume to 20 ml. The amount of ion exchange resin was caried from 0.02 to 0.4 g. In all experiments, the temperature was maintained constant at 20 ± 1°. For the radioactivity measurements, 1-ml samples of both the original solution and the equilibrium solution were evaporated to dryness.

The resulting data were plotted as a graph showing φ as a function of [A^-] (concentration of anion ligand). Values of φ^0 (φ for zero concentration of the ligand) were determined experimentally. For yttrium, $\varphi^0 = 18160 \pm 1200$; for cerium $\varphi^0 = 26170 \pm 2000$. The curves ($\log \varphi - \log [A^-]$) are shown in Fig. 1. Calculation of the stability constants of the complex compounds was carried out by the method of Fronaeus [7]. It was assumed that three forms of complexes were present in the solutions in the concentration range studied: MA^{2+}, MA_2^+, and MA_3; the simple ion M^{3+} was also assumed to be present. The expression for the distribution coefficient in such a system assumes the form:

$$\varphi = \frac{\varphi^0 + l_1\beta_1[A^-] + l_2\beta_2[A^-]^2}{1 + \beta_1[A^-] + \beta_2[A^-]^2 + \beta_3[A^-]^3}, \qquad (1)$$

where, β_1, β_2, and β_3 are the over-all stability constants of the complexes MA^{2+}, MA_2^+, and MA_3; and l_1 and l_2 are the distribution coefficients of the cationic complexes.

From the data showing the dependence of φ on [A^-] was calculated the function

$$\Phi_1 = \left(\frac{\varphi^0}{\varphi} - 1\right)\frac{1}{[A^-]},$$

the limit of which is

$$\lim_{[A^-]\to 0}\Phi_1 = \beta_1 - l, \text{ where } l = \frac{l_1\beta_1}{\varphi^0}.$$

The following function was then calculated

$$f = \beta_1\Phi_1 - \beta_2 - \beta_3[A^-]$$

or, in a different form,

$$f = \frac{\frac{\varphi^0}{\varphi}\{(\beta_1 - l)[A^-] - 1\} + 1}{[A^{-2}]}$$

with the limit $\lim_{[A^-]\to 0} f = f^0$.

The equation

$$\frac{\Delta f}{[A^-]} = \beta_1\frac{\Delta\Phi_1}{[A^-]} - \beta_3, \qquad (2)$$

where $\Delta f = f - f^0$ and $\Delta\Phi_1 = \Phi_1 - \Phi_1^0$ represents a straight line from which β_1 and β_3 may be determined by graphic means. On the basis of these data, the value of β_2 may be found from the equation $f^0 = \beta_1\Phi_1^0 - \beta_2$.

Corrected values of φ for each value of [A^-] were taken from the curves of φ vs. [A^-] shown in Fig. 1. They were used as indicated above. As an example, Fig. 2 shows the results of calculations made by means of Eq. (2) for yttrium α-hydroxyisobutyrate; according to these calculations $\beta_1 = (1.3 \pm 0.1) \cdot 10^3$; $\beta_2 = (4.0 \pm 0.6) \cdot 10^5$; $\beta_3 = (2.0 \pm 0.6) \cdot 10^7$. On the basis of these data, the contents of the various forms of complex compounds were calculated as functions of ligand concentration (Fig. 3).

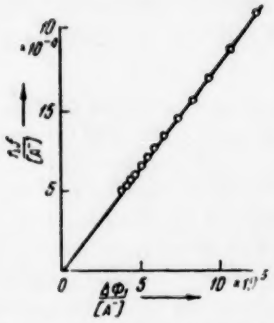

Fig. 2. Graphic representation of the equation $\frac{\Delta f}{[A^-]} = \beta_1 \frac{\Delta \Phi_1}{[A^-]} - \beta_3$ for yttrium α-hydroxyisobutyrate.

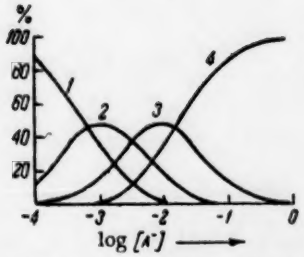

Fig. 3. Contents of the various complex compounds of yttrium and α-hydroisobutyric acid as functions of ligand concentration. 1) Y^{3+}, 2) YA^{2+}, 3) YA_2^+, 4) YA_3.

Values of the stability constants of complex compounds of Y and Ce with the acids studied were obtained in a similar manner (see the table).

Closely similar data appear in the literature. According to Paramonova [9], the constant for $YLac_2^+$ is $9.1 \cdot 10^4$, while according to reference [10], it is $5.0 \cdot 10^4$. The stability constant of $YLac^{2+}$ is $3.7 \cdot 10^2$ (all for an ionic strength of $\mu = 0.2$). Reference [11] reports the following values for an ionic strength of 0.5: $YLac^{2+}$ $4.36 \cdot 10^2$, $CeLac^{2+}$ $2.42 \cdot 10^2$ and $2.82 \cdot 10^2$, $CeLac_2^+$ $5.32 \cdot 10^3$.

It may be concluded that the strength of the bond of the hydrogen with the acid residue in the monobasic α-hydroxy acids is directly proportional to the strength of the bond of the rare earth element in the complex compound formed with the acid. This relationship is very apparent in the series glycolic–lactic–α-hydroxyisobutyric acids. For these acids, as for the corresponding yttrium complex compounds, we observed a relatively great difference in the values of the dissociation constants. In the case of α-hydroxyisovaleric acid, which falls between lactic and α-hydroxyisobutyric acids with respect to the strength with which the proton is bound and which lies closer to lactic acid, there was an anomalous shift in the stability of the yttrium complex compound toward a less stable complex. It is evident that the dimensions of the ligand affect to a significant extent the stability of the rare earth salts of α-hydroxyisovaleric acid. During the formation of complex compounds, steric hindrance and the very fact that the distance between the centers of the interacting ions is greater lead to a decrease in stability as compared to that with the preceding members of this series of α-hydroxy acids [8]. This factor has a still greater effect on the properties of cerium complex compounds, and this is apparently associated with the greater dimensions of Ce^{3+}. In the case of the formation of complex compounds of cerium with glycolic and lactic acids, the effect of ligand volume, on the one hand, and strength of the bond with the proton, on the other, are apparently mutually compensating. The strength of the bond of cerium with α-hydroxyisobutyric acid is very weak as compared to the strength of the corresponding bond in the yttrium complex.

Stability Constants (β) of Complex Compounds of Yttrium and Cerium with Certain α-Hydroxy Acids

	β	Glycolic acid	Lactic acid	α-Hydroxyisobutyric acid	α-Hydroxyisovaleric acid
Y	β_1	$(6,1\pm0,4)\cdot10^2$	$(6,8\pm0,5)\cdot10^2$	$(1,3\pm0,1)\cdot10^3$	$(4,0\pm0,3)\cdot10^2$
	β_2	$(5,1\pm0,7)\cdot10^4$	$(8,5\pm1,0)\cdot10^4$	$(4,0\pm0,6)\cdot10^5$	$(9,0\pm1)\cdot10^4$
	β_3	$(1,0\pm0,3)\cdot10^6$	$(6,0\pm2,0)\cdot10^6$	$(2,0\pm0,6)\cdot10^7$	$<1\cdot10^6$
Ce	β_1	$(2,7\pm0,3)\cdot10^2$	$(2,7\pm0,3)\cdot10^2$	$(2,7\pm0,3)\cdot10^2$	$(1,7\pm0,2)\cdot10^2$
	β_2	$(1,3\pm0,3)\cdot10^4$	$(1,3\pm0,3)\cdot10^4$	$(2,2\pm0,4)\cdot10^4$	$(3,2\pm0,6)\cdot10^3$
	β_3	$(2,0\pm1,0)\cdot10^5$	$(2,0\pm1,0)\cdot10^5$	$(2,0\pm1,0)\cdot10^5$	$(6,0\pm3,0)\cdot10^4$

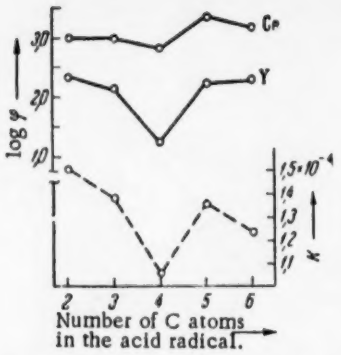

Fig. 4. Dependence of log φ for Y and Ce on the number of carbon atoms in the ligand (the value of log φ corresponds to log $[A^-] = -1.5$). The lower curve shows the dissociation constants of the α-hydroxy acids.

Finally, the complex of Ce^{3+} with α-hydroxyisovaleric acid is so unstable as compared to the yttrium complex that it is evident that the ligand volume is the determining factor in this case.

Figure 4, which presents additional data for α-hydroxyisocaproic acid, demonstrates graphically the role played by the volume of the ligand. Comparison with the values of the dissociation constants shows that the nature of the change in φ of yttrium and cerium with the first three acids is in good agreement with the change in the dissociation constant, while with the last two acids• there was a weakening of the complex bond owing to the volume of the ligand. This effect is not so sharply apparent in the case of cerium, owing to the relatively great volume of the cerium.

With respect to selection of optimum conditions for chromatographic separation of micro amounts of rare earth elements, the following conclusion may be made: The greater the strength of the bond with the proton in the α-hydroxy acid, i.e., the weaker the acid, the higher will be the value of the distribution coefficient of the rare earth element. From this point of view, α-hydroxyisobutyric acid is the best eluent, since it would be impossible to expect that subsequent members in the series of α-hydroxy acids would be stronger complex formers (or, correspondingly, weaker acids). Some improvement in separation may be expected with α-hydroxyisovaleric acid, for which there is a sharp decrease in the stability of the cerium complex owing to the greater volume of the ligand.

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•The dissociation constants of glycolic, lactic and α-hydroxyisobutyric acids were taken from the literature. The constants for α-hydroxyisovaleric and α-hydroxyisocaproic acids were determined by potentiometric titration; the accuracy of the determinations was sufficient for present purposes.

ALKYLATION OF 2-CHLOROANISOLE WITH PROPYLENE, 2-BUTENE, AND CYCLOHEXENE IN THE PRESENCE OF $BF_3 \cdot H_3PO_4$

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It is well known that alkylhaloanisoles are not readily available compounds, owing to the lack of simple methods of synthesis. We have shown in previous work that alkylation of 4-chloroanisole with propylene, 2-butene, and cyclohexene in the presence of $BF_3 \cdot H_3PO_4$ gives the corresponding mono- and dialkyl-4-chloroanisoles in over-all yields of from 90 to 100% of theoretical, depending on the conditions used. In further developing our investigation along this line, we have studied the reaction of 2-chloroanisole with propylene, 2-butene, and cyclohexene in the presence of the same catalyst. The reaction was studied under conditions which we had previously established as the most favorable for alkylation of 4-chloroanisole. It was found that, in contrast to alkylation of 4-chloroanisole, alkylation of 2-chloroanisole with these olefins gave only the monoalkyl-2-chloroanisoles. Furthermore, with propylene and 2-butene, the products were 4-alkyl-2-chloroanisoles, which, even during the first distillation, boiled within a 2° range and left almost no residue in the distillation flask (the residue was a brown tar, and comprised 0.2-0.4 g). The yield of these products was 96-97% of theoretical, i.e., somewhat higher than the over-all yield of mono- and dialkyl-4-chloroanisoles. In the case of cyclohexene, two monocyclohexyl-2-chloroanisoles, crystalline and liquid, were formed. When the first of these was heated for a number of hours with HI or HBr, it was demethylated to the corresponding cyclohexyl-2-chlorophenol, and the structure 4-cyclohexyl-2-chloroanisole was assigned to it. The liquid was not demethylated under analogous conditions, and did not crystallize at -20°. It is assumed that it was 6-cyclohexyl-2-chloroanisole. The relative content of the liquid in the crystalline isomer was 5.1% (5.4 g of liquid was separated from 105.4 g). The over-all yield of the ortho and para isomers varied from 93 to 98%, depending on conditions. They distilled together at 138-142°/3 mm, and left almost no residue (the residue in the flask was a brown liquid and amounted to 0.4-0.6 g).

EXPERIMENTAL

The 2-chloroanisole was prepared by diazotization of o-anisidine, the synthesis following that used for 4-chloroanisole [1]. It boiled at 66-67° at 2 mm, d^{20}_4 1.1927, $n^{20}D$ 1.5460. The propylene, 2-butene, cyclohexene, and catalysts were prepared as previously described [2]. The reaction was carried out in a manner similar to that used in the alkylation of 4-bromophenol with olefins [3].

1. Alkylation of 2-chloroanisole with propylene. The reaction mixture consisting of 88 g of 2-chloroanisole, 7.0 g of $BF_3 \cdot H_3PO_4$ and 8.6 g of propylene (3 : 1 : 0.2 mole ratio) was heated for 2 hr at 60° and then allowed to stand for 12 hr at room temperature. It was then treated in the usual manner and distilled. There was obtained 36.2 g, corresponding to a yield of 96% of theoretical, of 4-isopropyl-2-chloroanisole (I), which boiled at 91-92° at 3 mm, $n^{20}D$ 1.5242. The unreacted 2-chloroanisole amounted to 56.5 g, and the residue in the distillation flask, a brown tar, amounted to 0.4 g. Under analogous conditions, from 115.2 g of

2-chloroanisole, 10.6 g of $BF_3 \cdot H_3PO_4$, and 8.4 g of propylene (4 : 1 : 0.3 mole ratio) was obtained 35.5 g, 96.2% of theoretical, of product distilling at 93-94°/4 mm, 86.1 g of the original 2-chloroanisole, and 0.3 g of residue, a tar.

The 4-isopropyl-2-chloroanisole (I) was a colorless, oily liquid with an agreeable odor. When distilled a second time, it boiled at 91-92°/3 mm, and had d^{20}_4 1.0872, $n^{20}D$ 1.5245, MR_D: found, 51.92; calculated, 51.28.

Found %: Cl 19.17; 19.07
$C_{10}H_{13}OCl$. Calculated %: Cl 19.21

4-Isopropyl-2-chlorophenol (II) was obtained in 77.8% yield by heating (I) with hydrobromic acid for 45 hr. It was a colorless oily liquid. B.p. 70-71°/3 mm; d^{20}_4 1.1265, $n^{20}D$ 1.5336, MR_D: found, 47.02; calculated 46.55.

4-Isopropyl-2-chlorophenoxyacetic acid was prepared from (II) with a yield of 59.7%. It was obtained in the form of lustrous white plates. M.p. 72-73° (from petroleum ether).

2. Alkylation of 2-chloroanisole with 2-butene. The reaction mixture, consisting of 85.6 g of 2-chloroanisole, 7.9 g of $BF_3 \cdot H_3PO_4$ and 10.7 g of 2-butene (3 : 1 : 0.2 mole ratio), was heated for 3.5 hr at 60° and then allowed to stand overnight at room temperature; it was then treated in the usual manner and distilled. The yield of 4-sec-butyl-2-chloroanisole (III) was 36.4 g or 96.1% of theoretical; it boiled at 99-101°/4 mm and had $n^{20}D$ 1.5225. There was also obtained 58 g of unreacted 2-chloroanisole and 0.3 g of residue, a brown tar. When the reaction was carried out with 114.8 g of 2-chloroanisole, 10.4 g of $BF_3 \cdot H_3PO_4$ and 11.5 g of 2-butene (4 : 1 : 0.3 mole ratio) at the same temperature and a reaction time of 1 hr and 10 min, there was obtained 39.5 g or 97% of theoretical of (III), which distilled within the range 97-99°/3 mm, 84.9 g of unreacted 2-chloroanisole, and 0.2 g of a tarry residue.

The 4-sec-butyl-2-chloroanisole (III) was a colorless, oily liquid with a weak odor of anisole. B.p. 97-98°/2 mm, d^{20}_4 1.0700, $n^{20}D$ 1.5220, MR_D: found 56.59; calculated 55.90.

Found %: Cl 17.85; 17.64
$C_{11}H_{15}OCl$. Calculated %: Cl 17.84

4-Sec-butyl-2-chlorophenol (IV) was prepared in 76% yield by heating (III) with hydrobromic acid for 45 hr. It was a colorless liquid with a weak phenolic odor. B.p. 82°/3 mm, d^{20}_4 1.1061, $n^{20}D$ 1.5292, MR_D: found 51.45; calculated 51.28.

4-Sec-butyl-2-chlorophenoxyacetic acid was prepared from (IV) with a yield of 53.3%. M.p. 84-85°.

3. Cycloalkylation of 2-chloroanisole with cyclohexene. The reaction was carried out as described above. In each experiment, 0.1 mole of cyclohexene and the corresponding amount of 2-chloroanisole and $BF_3 \cdot H_3PO_4$ were used. The orthophosphoric acid was saturated with a 20-30% excess of boron trifluoride. The cyclohexene was added over a period of one hour; the mixture was then stirred for 2 hr and allowed to stand overnight at room temperature. The most characteristic experiments are summarized in the table.

The cycloalkylation products obtained in all experiments had almost completely crystallized after standing for a week at room temperature. Suction filtration of 105.4 g of product gave 5.4 g of liquid isomer.

The 4-cyclohexyl-2-chloroanisole (V) (the crystalline isomer) was in the form of white plates with an m.p. of 56° (from methyl alcohol.)

Found %: Cl 15.71; 15.61
$C_{13}H_{17}OCl$. Calculated %: Cl 15.78

4-Cyclohexyl-2-chlorophenol (VI) was obtained in 85.4% yield by heating (V) with hydrobromic acid for 45 hr. It had a b.p. of 122-123°/3 mm, d^{20}_4 1.1494, $n^{20}D$ 1.5544, MR_D: found, 58.75; calculated 58.58. It crystallized on standing. M.p. 39°. Literature values: b.p. 160.5°/12.5 mm, m.p. 41.5-42°, $n^{20}D$ 1.5578 [4]; b.p. 134.5°/2 mm, m.p. 53° [5].

4-Cyclohexyl-2-chlorophenoxyacetic acid was prepared from (VI) with a yield of 74.5%. M.p. 124-125° (from petroleum ether.)

Cycloalkylation of 2-Chloroanisole with Cyclohexene

Expt. No.	Mole ratio chloroanisole, cyclohexene, and $BF_3 \cdot H_3PO_4$	Temp., °C ± 2°	4- and 6-cyclohexyl-2-chloroanisoles				Residue, g.
			yield		boiling range, °C/mm	n_D^{20}	
			g	% of theoretical			
1	3 : 1 : 0,2	30	20,8	92,6	138—142/3	1,5474	0,6
2	3 : 1 : 0,3	60	21,0	93,5	139—142/3	1,5470	0,4
3	3 : 1 : 0,3	30	20,9	93,1	138—142/3	1,5475	0,5
4	3 : 1 : 0,3	20	20,7	92,2	138—142/3	1,5480	0,6
5	4 : 1 : 0,3	30	22,0	98,0	138—142/3	1,5475	0,4

The 6-cyclohexyl-2-chloroanisole (VII) (liquid isomer) had a b.p. of 124-126°/3 mm, d^{20}_4 1.1116, $n^{20}D$ 1.5410, MR_D: found 63.53; calculated 62.94. It did not crystallize on prolonged cooling at -20°. When heated with hydrobromic acid for 90 hr, it was practically quantitatively recovered unchanged.

Found %: Cl 15.73

$C_{13}H_{17}OCl$. Calculated %: Cl 15.78

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THE EFFECT OF CONJUGATION ENERGY ON THE RATE OF CATALYTIC DEHYDROGENATION OF ALKYLAROMATIC AND ALKYLHEXAHYDROAROMATIC HYDROCARBONS

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The catalytic dehydrogenation of alkylaromatic hydrocarbons with the formation of a bond conjugated with the benzene ring takes place at a significant rate, which depends on the structure of the alkyl radical. Thus, it was shown in previous work [1] that ethylbenzene and isopropylbenzene dehydrogenate readily over a mixed oxide catalyst, and the rate constant for dehydrogenation of isopropylbenzene, which has a branched alkyl radical, is twice the rate constant for the dehydrogenation of ethylbenzene (see Table 1). It therefore appeared to be of interest to determine whether an alkyl radical attached to a hexahydroaromatic ring will dehydrogenate. With this aim, we investigated the dehydrogenation of ethylcyclohexane and isopropylcyclohexane over this same catalyst.

Rate Constants for the Dehydrogenation of Alkylaromatic and Alkylhexahydroaromatic Hydrocarbons, $k_c \cdot 10^2$ g·min·ml

Temp., °C	Ethylbenzene	Isopropylbenzene	Ethylcyclohexane*	Isopropylcyclohexane*
520	0,285	0,776	—	—
540	0,5096	1,226	—	0,0333
550	0,783	1,572	0,04	—
560	1,055	—	—	0,0666
570	—	—	0,075	—

*In view of the low percentage conversions, these figures were used for calculation of the rate constants.

As is well known [2], hexahydroaromatic hydrocarbons are smoothly dehydrogenated over metals by a sextet mechanism [3]. It was shown in work reported in reference [4] that over chromium oxide, cyclohexane dehydrogenates to benzene by an edge mechanism. Cyclohexane is dehydrogenated to benzene in 50% yield over chromia–alumina catalyst at 440°; when ethylcyclohexane is passed over this catalyst at 400-450°, the reaction proceeds stepwise through successive dehydrogenation of the ring to ethylbenzene and dehydrogenation of the ethylbenzene to styrene, as we have shown previously. When ethylcyclohexane was passed over mixed chromia–alumina–tungsten and chromia–alumina–vanadia catalysts [6], styrene was obtained, and it was proposed that the reaction proceeds in two stages through ethylbenzene. In experiments which we carried out with cyclohexane, it was found that cyclohexane is not dehydrogenated by the same catalyst over which alkylbenzenes were dehydrogenated, but is recovered unchanged.

EXPERIMENTAL RESULTS AND DISCUSSION

The apparatus and experimental method have been described in a paper on the dehydrogenation of isopropylbenzene [1]. As before, the experiments were carried out with 10 ml of catalyst over the temperature interval 550-600°. The hydrocarbon feed rate was 0.5 ml in 3 min (which corresponds to a space rate of 1000 ml/liter/hour.) Steam dilution was in a ratio of 1 : 2.7-3.0 by weight. The catalyst was purged with a steam–air mixture and with air after each experiment. Experiments were carried out with cyclohexane (b.p. 81°, d^{20}_4 0.7783, $n^{20}D$ 1.4263), ethylcyclohexane (b.p. 129-130°, d^{20}_4 0.7854, $n^{20}D$ 1.4327), and isopropylcyclohexane (b.p. 153°, d^{20}_4 0.7939, $n^{20}D$ 1.4410). The catalyzate was analyzed for unsaturates content by Rosenmund bromometric titration [7].

As we remarked above, ethylcyclohexane did not dehydrogenate under these conditions. The constants of the catalyzate were the same as those of the original cyclohexane ($n^{20}D$ 1.4264). The ethylcyclohexane and isopropylcyclohexane dehydrogenated to a very slight extent. When ethylcyclohexane was passed over the catalyst at 550°, 1% vinylcyclohexane was found in the catalyzate; the attempted dehydrogenation of isopropylcyclohexane gave about 2% isopropylidenecyclohexane. With an increase in the temperature to 600°, the unsaturates content of the catalyzate increased to 3.8% and 6.7%, respectively, for these two hydrocarbons. At this same temperature, cracking of the hydrocarbons was observed with the formation of methylcyclohexane and light hydrocarbons (methane, ethane, and unsaturated hydrocarbons.)

The vinylcyclohexane was isolated from the catalyzate and characterized as the insoluble adduct with $HgAc_2$; the adduct had an m.p. of 218-220°. A mixed sample of this adduct and adduct prepared from vinylcyclohexane synthesized by another route showed no depression of the melting point. Data comparing the dehydrogenation rate constants for alkylaromatic and alkylhexahydroaromatic hydrocarbons are presented in Table 1.

These results show that the rate of catalytic dehydrogenation depends on the structure of the original hydrocarbon, its alkyl radical, and chiefly, on the possibility of forming a bond conjugated with the aromatic ring. Dehydrogenation of an alkyl group attached to a hexahydroaromatic ring is difficult.

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ON THE NATURE OF THE ALKYLATION OF AROMATIC HYDROCARBONS WITH OLEFINS IN THE PRESENCE OF $BF_3 \cdot H_3PO_4$

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In the opinion of the majority of investigators, benzene homologs react with olefins and other alkylating agents considerably more rapidly than does benzene [1-3]. However, analyzing the experimental results by means of equations describing successive processes [4], it is not difficult to become persuaded that this assumption is by no means invariably justified. Very frequently, and especially in the presence of acid catalysts, benzene is more easily alkylated than are monoalkylbenzenes, as a result of which the yield of the latter will be higher than when $AlCl_3$ is used, although in the first case dealkylation of polyalkylbenzenes does not occur [5,6].

On the basis of the most general concepts of the mechanism of Friedel-Crafts reactions, it may be assumed that the presence of alkyl groups on the benzene ring will strongly activate the substitution reaction only when the attacking reagent has a significant positive charge. In the contrary case, the activating effect of electronegative substituents is significantly weaker, and, since, stereochemical and probability factors do not favor alkylation of benzene homologs, benzene can exhibit greater reactivity.

For confirmation of this assumption and in order to establish a reactivity series for alkylbenzenes, we studied the following reactions in the presence of $BF_3 \cdot H_3PO_4$: alkylation of benzene and of binary mixtures of toluene with benzene, ethylbenzene, cumene, and o-, m-, and p-xylenes with propylene, cyclohexene, 1- and 2-butenes, and isobutene; alkylation of mixtures of benzene with ethylbenzene, cumene, and xylenes with butenes and cyclohexene; alkylation of mixtures of m-xylene with sec- and tert-butylbenzenes with propylene and 2-butene; alkylation of mixtures of benzene and tert-butylbenzene with cyclohexene; alkylation of cumene, diisopropylbenzene, and mixtures of the latter with benzene with propylene.

The original aromatic hydrocarbons were chemically pure substances, the physicochemical properties of which were in agreement with the literature values. The 2-butene was separated from a 2-butene–butadiene fraction, and the remaining olefins were prepared by dehydration of the corresponding alcohols [7]. The purity of the propylene and butenes was 96-99% (analysis was by the sulfuric acid method [7]), and the cyclohexene reacted quantitatively with a solution of bromine in chloroform. Prior to use, the n-butenes were purified from possible traces of isobutene by passage through a diffuser and bubble column filled with 70-72% H_2SO_4. The alkylation was carried out by a method which has already been described [8]. One mole of the aromatic hydrocarbons was used in each experiment. The reactivity of tert-butylbenzene with respect to the n-olefins and cyclohexene was determined at 20°. The remaining experiments were carried out over a period of 1-2 hr at 60° in the presence of 0.1 mole of $BF_3 \cdot H_3PO_4$ (except when the effect of various factors on the course of the process was under investigation). The alkylation of benzene and of mixtures of aromatic hydrocarbons with isobutene constituted an exception. In the first case, the reaction conditions were: temperature, 35-40°; catalyst

TABLE 1

Amts. of reactants, centimoles				Time, hours	Composition of hydrocarbon layer, centimoles					
benzene	toluene	propylene	$BF_3 \cdot H_3PO_4$		benzene	toluene	cumene	cymene	polyalkyl-benzenes	
50	50	50	10	1,0	23.6	31,4	24,8	17,8	2,4	0,62
25	75	50	10	0,8	10,3	43,8	14,1	29,7	2,1	0,61
65	35	50	10	0,9	33,2	22,1	32,8	12,2	2,7	0,60
50•	50	55	10	2,0	21,3	29,3	25,6	18,8	5,0	0,63
50•	50	41	10	0,7	26,5	33,9	22,5	15,5	1,6	0,61
40	60	50	20	1,0	17,8	36,4	21,0	22,6	2,2	0,62
50	50	50	5	4,0	23,8	31,0	24,1	17,8	3,3	0,64
48	52	45	3	1,5	25,1	34,3	20,8	16,2	3,6	0,63
50	50	50	10	6,0	23,2	31,1	24,9	18,3	2,5	0,62
50	50	26	10	0,5	35,1	40,3	14,6	9,4	0,6	0,62
30••	30	30	10	1,2	14,5	19,0	—	—	—	0,63

• The reactions were carried out at 30° and 80°, respectively, and the remainder at 60°.

••40 centimoles of cymene added to the alkylation mixture.

TABLE 2

Aromatic hydrocarbon	Relative alkylation rate •					Aromatic hydrocarbon	Relative alkylation rate •				
	with propylene	with 2-butene	with 1-butene	with isobutene	with cyclohexene		with propylene	with 2-butene	with 1-butene	with isobutene	with cyclohexene
Toluene	0.62	0.56	0.72	3.78	0.94	tert-Butyl-benzene	0.14	0.12	—	0.89	0.23
Ethyl-benzene	0.35	0.29	0.38	3.04	0.61	o-Xylene	0.45	0.40	0.49	7.51	1.07
Isopropyl-benzene	0.19	0.17	0.20	2.15	0.34	m-Xylene	0.38	0.31	0.39	0.68	0.58
						p-Xylene	0.32	0.26	0.34	0.0	0.46
sec-Butyl-benzene	0.17	0.16	0.17	—	—						

• Benzene alkylation rate = 1.

concentration, 10 mole %; time, 1-1.5 hr. In the second case the conditions were : temperature, 30°; catalyst concentration 5 mole % $BF_3 \cdot H_3PO_4$; time 0.6-1 hr. All of the results presented in Tables 2 and 3 were obtained under these standard conditions. The composition of the reaction products was established by rectification in a column of 25-30 theoretical plates; the cyclohexene content of the benzene fraction was determined bromometrically or refractometrically. The over-all loss during treatment of the reaction mixture did not exceed 1-2%, and it did not change the composition of the hydrocarbon layer, as was demonstrated by control experiments. Therefore, in calculating the relative reactivities of the aromatic hydrocarbons by means of the formula $r = \frac{K_A}{K_B} = \frac{\log A/A_0}{\log B/B_0}$, where A_0 and A, B_0 and B are the initial and final amounts of the substances used in the reaction and K_A and K_B are the corresponding alkylation rate constants. We assumed that the losses were proportional for all of the components of the hydrocarbon layer.

In order to determine the extent of the effect of dialkylation on the composition of the alkylate, special experiments were carried out, and these showed that only hydrocarbons with tert-butyl groups underwent appreciable

TABLE 3

Composition of Products from the Alkylation of Aromatic Hydrocarbons•

Compound alkylated	Olefin	Mole ratio of olefin to arom. hydrocarbon	Composition of hydrocarbon layer, mole %									
			benzene		alkylbenzenes							
					mono-		di-		tri-		tetra-	
			expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
Benzene	Propylene	0.20	80.5	80.4	19.0	19.2	0.5	0.4	–	–	–	–
		0.59	52.9	52.7	43.9	44.3	3.2	3.0	–	–	–	–
		1.00	16.0	16.2	68.1••	67.7	15.9	15.6	–	0.5	–	–
		1.55	0.9	1.0	51.4	51.1	40.2	41.0	6.8	6.5	0.7	0.6
		2.21	–	–	16.3	14.6	51.3	52.5	27.5	28.2	4.9	4.7
Isopropyl-benzene		0.57	–	–			43.0	42.9	6.5	6.7	0.4	0.3
		1.29	–	–	59.1	50.1	51.2	51.8	30.4	30.1	5.6	5.5
Diisopropyl-benzene		0.32	–	–	12.8 –	12.6 –	70.5	70.6	27.0	26.8	2.5	2.6
Benzene and diisopropyl-benzene (69.6 : 30.4)		0.50	25.6	25.6	39.4	39.4	33.8	–	1.2	–	–	–
Benzene	2-Butene	0.24	76.2	76.2	23.2	23.2	0.6	0.6	–	–	–	–
	1-Butene	0.86	24.8	25.0	64.9	64.5	10.3	10.5	–	–	–	–
	2-Butene	0.45	57.5	57.6	40.5	40.3	2.0	2.1	–	–	–	–
	1-Butene	1.34	2.2	2.4	62.0	61.6	35.8	36.0	–	–	–	–
	Isobutene	0.31	70.6	70.7	24.8	24.7	4.6	4.6	–	–	–	–
	Isobutene	0.66	51.1	51.3	35.9	35.5	13.0	13.2	–	–	–	–
	Cyclohexene	0.35	67.2	67.3	30.9	30.7	1.9	2.0	–	–	–	–
	Isobutene	0.97	22.6	22.4	56.3	58.7	19.1	18.9	–	–	–	–

• The relative reactivities of cyclohexylbenzene, tert-butylbenzene, sec-butylbenzene, mono-, di-, and triisopropylbenzenes in corresponding reactions were: 0.31, 0.89, 0.116, 0.185, 0.074, and 0.037. The calculations were carried out by means of the equation for successive reactions [4].

••From the experimental data of Topchiev and coauthors [9].

dealkylation. Furthermore, the rate of this process depended only on the concentration of the substance dealkylated and on the temperature. The dealkylation rate constant of di-tert-butylbenzene was 0.1 hour^{-1} at 50° and 0.015-0.017 hour^{-1} at 30-35°. The other alkylbenzenes studied had rate constants of the order of 0.033-0.008 at 60-80°, and, consequently, they underwent no change during the reaction time used (1-2 hr).

Identification of the alkylation products and determination of the orientation of substituents in polyalkylbenzenes were carried out both by the usual methods and by means of infrared absorption spectroscopy.

Some of the experiments on the alkylation of benzene–toluene mixtures are shown in Table 1; the values of the toluene reactivity, $\bar{r}$, are equal to the ratio of the rate constants for propylation of toluene to those for benzene. It may be seen from these data that reaction conditions and reagent ratios do not have a great effect on the value of $\bar{r}$. Similar results were obtained during alkylation of the other hydrocarbons with propylene, n-butylenes, and cyclohexene. Only in the case of the reaction of benzene and its homologs with isobutene was there observed some effect of temperature and of reaction time on the ratio of the rate constants; this was associated with disproportionation of the tertiary butyl groups and possibly with the great difference in the activation energies of competitive reactions.

Values of the relative reactivities of benzene homologs with respect to the different olefins are summarized in Table 2.

The $BF_3 \cdot H_3PO_4$ catalyst not only did not of itself cause any considerable disproportionation of primary and secondary alkyl radicals, but during the course of the alkylation reaction it did not form "peculiar complexes" which would dealkylate the polyalkylbenzenes. In fact, the addition of the latter to the alkylation mixture not only does not increase the yield of monoalkylbenzenes [5], which could result as a consequence of polymerization of the olefin or alkylation of part of the added substance, but in our case it did not change the ratio of the rate constants calculated from the composition of the reaction mixture (see Tables 1-3). Moreover, r has a single value (within the limits of experimental error, ± 2%) regardless of the mixtures used in their determination; i.e., the so-called solvent effect had no substantial influence in the present case. This fact found confirmation in the results of alkylation of individual hydrocarbons with olefins; the ratio of the rate constants of successive reactions did not depend on the extent of alkylation of the aromatic hydrocarbon (see Table 3), which suggests the possibility of rather accurately predicting the composition of an alkylate.

While "external" factors had almost no effect on the relative reaction rates of benzene homologs, the nature of the alkylating agent determines these values to no less an extent than does the structure of the aromatic hydrocarbon itself. The majority of the alkylbenzenes studied in the present work were alkylated by isobutene much more readily than was benzene in spite of the practically complete absence of butylation in the ortho and meta positions to the alkyl group. Propylene, the n-butenes, and cyclohexene, on the contrary, reacted more rapidly with benzene than with its homologs. Moreover, the Baker-Nathan series was followed in all cases, which is due to the significant extent of hyperconjugation. We will not discuss in detail the hyperconjugation effect, since this question is not new. We remark only that the lack of basis for the opinions of those authors who explain the differences in the alkylation rates of toluene, ethylbenzene, cumene, and tert-butylbenzene by hindrance arising during alkylation in the ortho position [3] is graphically emphasized by the results of the alkylation of these hydrocarbons with isobutene (see above). In interpreting the series of regularities [primarily the greatly decreased activity of the meta position of alkylbenzenes (as compared to any of the six positions of benzene), but also the low relative rates of alkylation of cumene and the butylbenzenes by n-olefins] it must be recognized that alkyl groups create hindrance not only during ortho substitution, but also during meta and para substitution (this is probably connected with difficulty in solvating the transition complex). Of course, as a consequence of the increase in density of the electron cloud in the alkylbenzene molecule and the ease of polarization of the latter at the instant of reaction, the effect of unfavorable factors will be moderated or even overshadowed. However, on the whole, alkylbenzenes can react more rapidly than benzene only with those olefins which are strongly polarized by the catalyst, forming ions with a higher effective charge centered on the reacting carbon atom. As a matter of fact, of the olefins studied only isobutene, which is generally known to polarize readily, preferentially alkylates benzene homologs. On changing to cyclohexene and, further, to 1-butene, propylene, and 2-butene, the value of r regularly decreases, and this may be explained by the decrease in the activity of the attacking agents. The difference in the relative reactivities of the alkylbenzenes with respect to 1- and 2-butene merits attention. This fact persuasively shows that rupture of a π-bond during alkylation proceeds gradually along with the formation of the bond with the aromatic ring. If polarization of the olefins did proceed as far as the formation of free carbonium ions, this difference would not be observed, since both butenes yield identical ions in the limiting case. In our opinion, the specific catalytic action of $BF_3 \cdot H_3PO_4$ and certain other acid catalysts are explained by a crypto-ionic mechanism for the alkylation reaction.

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SOME NEW ADDITION REACTIONS OF ACETYLENECARBOXYLIC ACIDS AND THEIR ESTERS

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During the course of our work on the synthesis of compounds which are potentially physiologically active, we have carried out reactions of acetylenecarboxylic acids with: a) arenesulfinic acids, b) cyclic thioamides, and c) cyclic amines.

a) Reaction of acetylenedicarboxylic acid (ADC) and its esters with arenesulfinic acids. ADC and its esters are similar to benzoquinone in many reactions. Evidently, this is connected with the presence in these compounds of related conjugated systems ($O=\overset{|}{C}-C\equiv C-\overset{|}{C}=O$ and $O=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O$). Thus, like quinone [1-5], ADC adds alcohols and phenols [6, 7], mercapto compounds [8, 9], and amines [10, 11]. One of the characteristic reactions of benzoquinone is the addition of arenesulfinic acids [12, 13]. As far as we are aware, no similar reaction is described in the literature for ADC. It was found that ADC reacts with arenesulfinic acids when heated in glacial acetic acid; the methyl and ethyl esters of ADC react similarly, but in methanol solution. This reaction yielded crystalline sulfones which, according to the analytical data, were products of the addition of two molecules of the sulfinic acid to ADC.

When heated with a solution of potassium hydroxide, these disulfones hydrolyzed smoothly, splitting off the sulfinic acids, which were identified as their adducts with benzoquinone. The disulfones prepared from esters of ADC (compounds 2, 3, 4, and 6, Table 1) readily reacted with Na, which indicates the presence of an "acidic" hydrogen in the group

$$-OC-\overset{|}{C}H-SO_2-.$$

The infrared spectra of compounds 1, 2, 4, and 5 had strong absorption bands in the regions of 1335-1320 cm^{-1} and 1154-1150 cm^{-1}, which are characteristic of asymmetrical and symmetrical vibrations of the SO_2 group [15]. The spectrum of compound 1 (Table 1) contained no band in the region of 1464-1407 cm^{-1}; such a band would be assigned to scissoring vibrational modes of the CH_2 groups [15]. All of this suggests that the addition products have structure I* (Table 1).

b) Reactions of acetylenecarboxylic acids and their esters with cyclic thioamides. It appeared to be of interest to determine whether compounds containing a potential thiol group, more specifically, cyclic thioamides such as benzthiazol-2-thione and benzimidazol-2-thione, will react with acetylenecarboxylic acids in a manner similar to mercaptans. We carried out the interaction of these thiones with ADC and its esters and also with

*Addition to both carbon atoms of the triple bond of ADC also takes place in other cases, for example, during the reaction of ADC and its methyl ester with thioacetic acid [14].

TABLE 1

Products of the Addition of Arenesulfinic Acids to Acetylenedicarboxylic Acid and Its Esters ROOC–CH(SO_2Ar)–CH(SO_2Ar)–COOR (I)

Expt. No.	R	Ar	Name	M.p., °C	Yield, %	Molec. formula	C, %		H, %		N, %	
							found	calc.	found	calc.	found	calc.
1	H	C_6H_5	α,α'-Di(phenylsulfonyl)succinic acid	189–190° (decomp.)	31	$C_{16}H_{14}O_8S_2$	48.28	48.30	3.29	3.52	15.95	16.07
2	CH_3	C_6H_5	Dimethyl α,α'-di(phenylsulfonyl)succinate	172–174	38	$C_{18}H_{18}O_8S_2$	50;45	50.75	4.11	4.23	15.10	15.05
3	C_1H_5	C_6H_5	Diethyl α,α'-di(phenylsulfonyl)succinate	124–126	34	$C_{20}H_{22}O_8S_2$	52.74	52.80	4.77	1.81	11.03	14.10
4	H	C_6H_5	α,α'-Di(p-tolylsulfonyl)cinnamic acid	182–184 (decomp.)	33	$C_{18}H_{18}O_8S_2$	50.51	50.75	4.01	4.23	15.00	15.05
5	CH_3	p-CH_3–C_6H_4	Dimethyl α,α'-di(p-tolylsulfonyl)succinate	170–172	67	$C_{20}H_{22}O_8S_2$	52.90	52.80	4.88	4.81	11.06	14.10
6	C_2H_5	p-CH_3–C_6H_4	Diethyl α,α'-di(p-tolylsulfonyl)succinate	164–166	95	$C_{22}H_{26}O_8S_2$	54.74	54.70	5.14	5.40	13.30	13.28
7	H	p-NO_2–C_6H_4	α,α'-Di(p-nitrophenylsulfenyl)cinnamic acid	192–194 (decomp.)	76	$C_{16}H_{12}O_{12}N_2S_2$ *	39.51	39.33	2.61	2.46	12.89	13.20

*Found %: N, 5.65; calculated %: 5.73.

TABLE 2

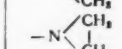
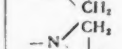
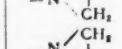
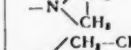
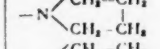
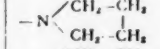
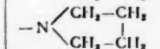
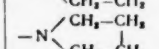
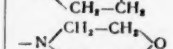
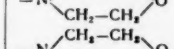
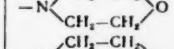
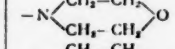
Products of the Addition of Cyclic Thioamides to Acetylenecarboxylic Acids and Their Esters

Expt. No.	R	R′	X	Name	M.p., °C	Yield, %	Molec. formula	N, %		S, %	
								found	calc.	found	calc.
1	H	H	S	β(2-Benzthiazolylthio)acrylic acid	190—191 (decomp.)	57	$C_{10}H_7O_2NS_2$ •	5.70	5.89	27.15	26.96
2	H	C_2H_5	S	Ethyl-β-(2-benzthiazolylthio)acrylate	78—80	55	$C_{12}H_{11}O_2NS_2$ ••	5.05	5.28	24.31	24.15
3	H	H	NH	β-(2-Benzimidazolylthio)acrylic acid	198—200 (decomp.)	63	$C_{10}H_8O_2N_2S$	12.72	12.73	14.50	14.51
4	H	C_2H_5	NH	Ethyl β-(2-benzimidazolylthio)acrylate	177—178	59	$C_{12}H_{12}O_2N_2S$	11.37	11.22	12.94	12.80
5	COOH	H	S	2-Benzthiazolylthiofumaric acid	154—156 (decomp.)	67	$C_{11}H_7O_4NS_2$	5.22	4.98	22.73	22.75
6	COOH	H	NH	2-Benzimidazolylthiofumaric acid	196—197 (decomp.)	80	$C_{11}H_8O_4N_2S$	10.76	10.60	12.16	12.12

• Found %: C 50.81; H 2.83. Calculated %: C 50.60; H 2.95.
•• Found %: C 54.33; H 4.35. Calculated %: C 54.30; H 4.15.

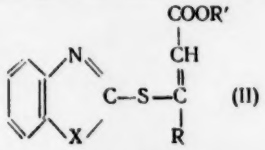
TABLE 3

Products of the Addition of Cyclic Amines to Acetylenecarboxylates R–C ≡ CH–COOR' (II[1])

Expt. No.	R	R'	–N<	Name	B. p., °C/mm	M.p., °C	Yield, %	Molec. formula	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
1	H	C_2H_5		Ethyl β-(N-ethylenimino)-acrylate •	65–67/3	–	51	$C_7H_{11}O_2N$	59.83	59.60	8.10	7.80	9.41	9.93
2	CH_3	C_2H_5		Ethyl β-(ethylenimino)crotonate ••	75–76/3	–	59	$C_8H_{13}O_2N$	62.07	61.80	8.60	8.38	9.31	9.01
3	C_6H_5	C_2H_5		Ethyl β-(N-ethylenimino)-cinnamate •••	135–136/3	–	71	$C_{13}H_{15}O_2N$	71.85	71.90	6.95	6.92	6.46	6.15
4	$COOCH_3$	CH_3		Dimethyl N-ethyleniminofurarate	–	71–72	16	$C_8H_{11}O_4N$	51.52	51.89	6.11	5.95	7.57	7.57
5	H	C_2H_5		Ethyl β-(N-pyrrolidyl)acrylate	–	41–43	55	$C_9H_{15}O_2N$	63.82	13.80	8.99	8.85	8.05	8.25
6	CH_3	C_2H_5		Ethyl β-(N-pyrrolidyl)crotonate	–	28–30	70	$C_{10}H_{17}O_2N$	65.52	65.55	9.35	9.28	7.51	7.61
7	C_6H_5	C_2H_5		Ethyl β-(N-pyrrolidyl)cinnamate	–	58–60	78	$C_{15}H_{19}O_2N$	73.31	73.46	7.84	7.75	5.98	5.71
8	$COOCH_3$	CH_3		Dimethyl N-pyrrolidylfumarate	–	69–71	54	$C_{10}H_{15}O_4N$	56.05	56.30	6.80	7.01	6.72	6.57
9	H	C_2H_5		Ethyl β-(N-morpholyl)acrylate	–	29–31	67	$C_9H_{15}O_3N$	58.15	58.30	8.41	8.11	7.92	7.56
10	CH_3	C_2H_5		Ethyl β-(N-morpholyl)crotonate	–	31–33	69	$C_{10}H_{17}O_3N$	60.26	60.25	8.56	8.54	7.31	7.02
11	C_6H_5	C_2H_5		Ethyl β-(N-morpholyl)cinnamate	–	49–51	68	$C_{15}H_{16}O_5N$	68.97	68.98	7.50	7.28	5.66	5.37
12	$COOCH_3$	CH_3		Dimethyl N-morpholylfumarate	–	57–59	52	$C_{10}H_{16}O_5N$	52.29	52.48	6.67	6.54	5.85	6.11

• $n^{20}D$ 1.4843, d^{20}_4 1.0277. •• $n^{20}D$ 1.4938, d^{20}_4 1.0040. ••• $n^{20}D$ 1.5673, d^{20}_4 1.0817.

propiolic acid and one of its esters; the reaction was run by heating in ethyl acetate or EtOH. This yielded readily crystallizable substances which proved to be products of the addition of one molecule of the cyclic thioamide to the acetylenecarboxylic acid or ester; the products had the structure (II) (Table 2).



(II)

Infrared spectra obtained for compounds 1, 3, 5, and 6 (Table 2) in the region 1900-800 cm^{-1} had absorption bands at 960-920 cm^{-1}, which are assigned to CH vibrations at a trans-substituted double bond [15]; weak bands in the region of 700-670 cm^{-1} were also found, and these are assigned to valence vibrations of the sulfide group [16]. It has thus been shown that cyclic thioamides can enter into addition reactions to give derivatives having a thiol form. Since any substantial shift of the thione form to the equilibrium thiol form is improbable under the experimental conditions used, it is obvious that the reaction proceeds with "transfer of the reaction center" [17].

c) Reaction of esters of acetylenecarboxylic acids with cyclic secondary amines. There are brief reports in the literature of the addition of piperidine to esters of acetylenecarboxylic acids [6, 11, 18, 19]. Reactions with other cyclic secondary amines have not been described. We carried out reactions of esters of acetylenedicarboxylic, tetrolic, propiolic, and phenylpropiolic acids with ethylenimine, pyrrolidine, and morpholine. In connection with the analogy, mentioned above, of ADC to benzoquinone, these compounds (particularly the compounds with ethylenimine) should be of interest, since ethyleniminobenzoquinones exhibit antitumor action [20].

The reactions were carried out by interacting the amines with the acetylenecarboxylic acid esters in the cold. The resulting products were colorless, viscous oils which crystallized on standing to low-melting crystalline substances.* The elemental composition of these substances did not change during the transition from the liquid to the crystalline state. The infrared data suggested that the liquid products had cis structures, and crystallization was associated with transition to the trans form. (The solid substances had absorption bands in the region of 990-960 cm^{-1}, which is characteristic of CH at a double bond with trans groups [15].) On the basis of the elemental analyses, the general formula (III) (Table 3) is assigned to these products.

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*Products of the reaction of ethylenimine with esters of propiolic, tetrolic, and phenylpropiolic acids (compounds 1-3, Table 3) constitute an exception; these compounds did not crystallize.

**Original Russian pagination. See C. B. translation.

FORMATION OF THE 1, 2, 3-OXADIAZINE RING BY THE INTERACTION OF 1, 1'-DIACETYLFERROCENE WITH AROMATIC DIAZONIUM COMPOUNDS

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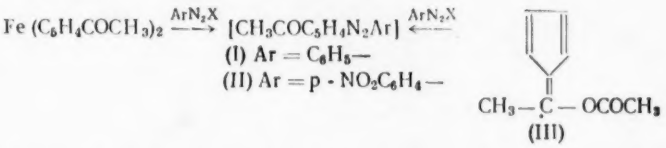
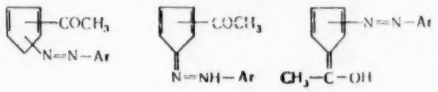
It is well known that aromatic diazo compounds arylate ferrocene with the formation of mono-, di-, and polyarylferrocenes [1, 2, 3]. As we have shown previously [4], 1,1'-diacetylferrocene reacts with diazo compounds in a completely different manner: the ferrocene ring is broken, and compounds are formed which do not contain iron. According to the carbon, nitrogen, and hydrogen contents, these compounds are arylazoacetocyclopentadienes, but their structure was not established.

In the present work, these compounds (I, II) were synthesized by a different route, their properties were studied, and a structure corresponding to substituted 1, 2, 3-oxadiazines is proposed for them. We found that the action of aromatic diazonium salts on the acetate of the enol form of acetylcyclopentadiene (III), which has been described by Riemschneider and Krüger [5], resulted in the formation of intensely colored substances identical with those formed from 1,1'-diacetylferrocene:



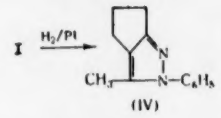
On the basis of their method of preparation and of the elemental composition of compounds I and II, it is possible to propose one of the following structures for these compounds:



However, a study of the properties of these substances showed that they are not arylazoacetocyclopentadienes. Compounds I and II are completely stable; they do not form derivatives characteristic of the presence of either a ketonic [4] or a hydroxyl group; a qualitative test for enols was negative. The infrared spectra of I and II showed no bands corresponding to C = O, C—OH and N—H groups. The presence of an intense band at 1563-1590 cm^{-1} indicated the presence of the conjugated bond system C = C—C = N. The dipole moment• of I in benzene was 1.70 D, which excludes the possibility of a polar structure, for example, of the ylide type. (I) formed a complex with cadmium chloride in a manner similar to isoxasoles.

•We desire to express our appreciation to Ya. K. Syrkin and E. A. Shott-L'vova for measuring the dipole moment.

When (I) was catalytically hydrogenated over Pt, 2 moles of hydrogen were absorbed, and the I was converted to 5-methyl-3,4-cyclopentano-1-phenylpyrazole (IV):

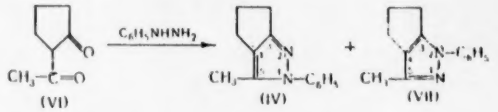


(IV)

Hydrogenation of II was accompanied by reduction of the NO_2 group and the formation of 5-methyl-3,4-cyclopentano-1-(p-aminophenyl)pyrazole (V).

The formation of substituted pyrazoles (IV and V) during the hydrogenation of I and II indicates that the five-membered carbon ring is retained during the interaction of 1,1'-diacetylferrocene and an aromatic diazonium compound and that the reaction takes place alpha to the acetyl group.

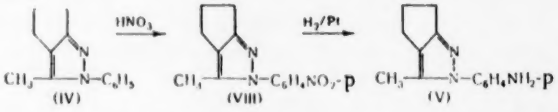
The structure of pyrazole IV was proved by alternate synthesis from acetylcyclopentanone (VI) and phenylhydrazine:



(VI) (IV) (VII)

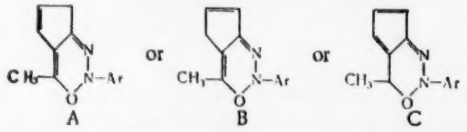
The interaction of phenylhydrazine with VI formed a mixture of the isomeric pyrazoles IV and VII in a yield of 95% of theoretical; these were separated chromatographically. The amount of the isomer identical with that formed during the hydrogenation of substance I was only 2.5% of the mixture. The isomer could only be 5-methyl-3,4-cyclopentano-1-phenylpyrazole (IV), since the phenyl group in the pyrazole formed by hydrogenation of I had to be in the 1 position, inasmuch as the original compound I was obtained by a reaction involving a benzenediazonium compound.

Nitration of 5-methyl-3,4-cyclopentano-1-phenylpyrazole (IV) gave 5-methyl-3,4-(p-nitrophenyl)pyrazole (VIII), catalytic reduction of which gave the corresponding p-aminophenylpyrazole (V), which was identical to that obtained during hydrogenation of II.



(IV) (VIII) (V)

The above facts provide a basis for the assumption that a 1,2,3-oxadiazine ring is present in compounds I and II and that these substances are substituted 1,2,3-oxadiazines:



A B C

The formation of pyrazoles during the hydrogenations is an argument (though not a decisive one, since isomerization is a possibility) in support of structures A and B.

EXPERIMENTAL

Interaction of the acetate of the enol form of acetylcyclopentadiene [5] (III) with benzenediazonium chloride. An alcoholic solution of 13.3 g (0.088 mole) of III was added gradually and with stirring to a solution of benzenediazonium chloride prepared from 0.1 mole of aniline. Stirring was continued for a period of 5 hr, after which the alcohol was distilled under vacuum. The residue was repeatedly extracted with benzene. The benzene solution was diluted with petroleum ether, and then chromatographed on Al_2O_3 deactivated in air for 2 hr and then on Al_2O_3 deactivated in air for 1 hr. Elution was carried out with a mixture of benzene and petroleum ether (1 : 4). There was obtained 6.0 g (32% of theoretical) of substance I in the form of beautiful bright red crystals. The melting point was 72-73° (from petroleum ether.)

Found %: C 73.33; 73.58; H 5.92; 5.80; N 13.08; 12.86

$C_{13}H_{12}N_2O$. Calculated %: C 73.56; H 5.69 N 13.20

Infrared spectrum (in vaseline oil and a polyfluorohydrocarbon, NaCl prism): 1563, 1488, 1422, 1375, 1352 1279, 1252, 1190, 1163, 1074, 1060, 1028, 935, 853, 764, 754, and 674 cm^{-1}.

Ultraviolet spectrum (in $CHCl_3$): λ_{max} 262, 422, 477 (log ϵ 4.41, 4.15, 4.21).

A mixture of this material with the substance formed by the interaction of 1,1'-diacetylferrocene and benzenediazonium chloride [4] melted without depression of the melting point. These two substances were identical with respect to their infrared spectra and their paper chromatograms [in an ethanol–formamide (1 : 1) system on Leningrad chromatographic paper impregnated with a 30% solution of formamide in methanol and partially dried in air (5 min) R_f = 0.67].

Interaction of III with p-nitrobenzenediazonium chloride. A solution of p-nitrobenzenediazonium chloride, prepared from 0.003 mole of p-nitroaniline, was added gradually and with stirring to an alcoholic solution of 0.5 g (0.003 mole) of III. After an hour, the precipitate was filtered, washed with water, dried, extracted with benzene, and chromatographed on Al_2O_3 deactivated in air for 2 hr. There was obtained 0.2 g (26% of theoretical) of substance II in the form of dark crimson crystals. The melting point was 204-205° (with decomposition, from benzene.)

Found %: C 60.32; 60.51; H 4.24; 4.23; N 15.75; 15.88

$C_{13}H_{11}O_3N_3$. Calculated %: C 60.69; H 4.31 N 16.34

Infrared spectrum (in vaseline oil and a polyfluorohydrocarbon, NaCl prism): 1590, 1560, 1515, 1429, 1370, 1332, 1313, 1279, 1248, 1212, 1187, 1164, 1106, 1072, 1057, 1020, 935, 870, 844, 804, 764, 748, and 687 cm^{-1}.

A mixture of this material with the substance previously obtained by us from diacetylferrocene [4] melted without depression of the melting point. The infrared spectra of these two substances were identical.

Complex of substance I with $CdCl_2$. To a solution of 0.1 g (0.00047 mole) of $CdCl_2 \cdot 2H_2O$ in 0.1 ml of warm water was added a fivefold volume of alcohol, and the resulting solution was poured into a saturated solution of 0.1 g (0.00047 mole) of I. The brown, acicular crystals which precipitated over a 48 hr period were filtered off, washed with alcohol, and dried under vacuum. The weight was 0.14 g. Another 0.04 g of complex was separated from the filtrate. The over-all yield of the complex of I with $CdCl_2$ was 0.18 g (quantitative). The complex of I with $CdCl_2$ did not melt, but decomposed at 240-250°; treatment with water gave a quantitative yield of I.

Found %: C 39.21; 39.15; H 2.85; 2.74; N 7.10; 7.24; Cl 17.55; 17.91

$C_{13}H_{12}N_2OCdCl_2$. Calculated %: C 39.47; H 3.06 N 7.08 Cl 17.93

Hydrogenation of I. The hydrogenation of 4.58 g (0.021 mole) of I was carried out in glacial CH_3COOH (70 ml) over platinum (from 0.07 g of PtO_2). A total of 1186 ml of H_2 (0.048 mole, 17°, 741 mm) was absorbed over the course of 9 hr. The solution was filtered, diluted with 300 ml of water, neutralized with 20% alkali, and repeatedly extracted with ether. The ethereal solution was dried with $MgSO_4$. The ether was distilled under vacuum. The residue was repeatedly extracted with n-pentane. The 5-methyl-3,4-cyclopentano-1-phenylpyrazole (IV), which remained after evaporation of the n-pentane, was distilled under vacuum (2 mm, bath temperature 120°). The yield was 2.77 g (65% of theoretical). The melting point was 78-79°. The IV was a white crystalline substance, readily soluble in organic solvents (somewhat less so in petroleum ether) and in acids.

Found %: C 79.04; 79.05; H 7.14; 7.14; N 13.95; 14.09

$C_{13}H_{14}N_2$. Calculated %: C 78.75; H 7.12; N 14.13

Infrared spectrum (in vaseline oil, NaCl prism): 700, 763, 909, 1022, 1057, 1360, 1458, 1506, 1590, and 2920 cm^{-1}.

Hydrogenation of II. The hydrogenation was carried out in a manner similar to that described above. From 2.4 g (0.009 mole) of II was obtained 1.2 g (66% of theoretical) of 5-methyl-3,4-cyclopentano-1-

(p-aminophenyl)pyrazole (V). The V was readily soluble in acids, hot water, $CHCl_3$, and alcohol, less so in benzene, and difficultly soluble in petroleum ether; it was crystallized from a mixture of benzene and petroleum ether. The melting point was 135-136°.

Found %: C 73.63; 73.37; H 7.27; 7.13; N 19.27
$C_{13}H_{15}N_3$. Calculated %: C 73.21; H 7.08; N 19.70

Synthesis of IV and VII from acetylcyclopentanone (VI) [6] and phenylhydrazine. To a solution of 8.6 g (0.08 mole) of freshly distilled phenylhydrazine in 11 ml of 28% H_2SO_4 was gradually added 10.1 g (0.08 mole) of VI. The mixture was heated for 2 hr at 90-95°; it was then neutralized with 10% NaOH and extracted with ether. From the ether solution was separated 15 g of a mixture of IV and VII (yield 95% of theoretical). A 6.0-g sample of this mixture was chromatographed on Al_2O_3. The VII was eluted with petroleum ether. The yield was 5.85 g (97.5% of the mixture). The melting point was 57-58° (from petroleum ether).

Found %: C 78.60; 78.61; H 7.26; 7.21
$C_{13}H_{14}N_2$. Calculated %: C 78.75; H 7.12

The IV was eluted with benzene. The yield was 0.15 g (2.5% of the mixture). The melting point was 78-79°. A mixture with a sample of IV prepared by hydrogenation of I melted without depression of the melting point. The infrared spectra of these two preparations were identical.

5-Methyl-3,4-cyclopentano-1-(p-nitrophenyl)pyrazole (VIII). A total of 0.3 g (0.0015 mole) of IV was introduced portionwise into ice-cooled HNO_3, sp. gr. 1.51 (3 ml). After 2 hr, the solution was poured into 50 ml of ice water. The VIII separated as a yellow precipitate. The yield of VIII was 0.3 g (83% of theoretical). VIII was readily soluble in acetone and $CHCl_3$ and somewhat less so in benzene and ether; it was crystallized from alcohol and from aqueous alcohol. The melting point was 137-138°.

Found %: C 64.15; 63.96; H 5.62; 5.64
$C_{13}H_{13}N_3O_2$. Calculated %: C 64.18; H 5.38

Reduction of 5-methyl-3,4-cyclopentano-1-(p-nitrophenyl)pyrazole (VIII). Hydrogenation of 0.66 g (0.0027 mole) of VIII was carried out in alcohol at room temperature over Pd black; hydrogenation time was 8 hr. The alcohol was distilled under vacuum under N_2. The yield of 5-methyl-3,4-cyclopentano-1-(p-aminophenyl)pyrazole (V) was 0.57 g (quantitative.) The melting point was 136-136.5° (after recrystallization from water and petroleum ether.) A mixture with a sample of the substance prepared by hydrogenation of II melted without depression of the melting point.

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PREPARATION OF ARYL HALIDES FROM AROMATIC HYDROXY COMOUNDS

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The simplest method of preparing aryl halides is by direct halogenation of aromatic hydrocarbons (ArH). However, this method has two intrinsic disadvantages, namely: Its application is limited, and halogenation proceeds in several directions. For example, it is practically impossible to prepare β-halonaphthalenes, m-halotoluenes, or o-halobiphenyls by direct halogenation of the aromatic hydrocarbons. Furthermore all aryl halides prepared by this route (with the exception of halobenzenes) are mixtures of the corresponding position isomers (usually with a predominance of one of them), and separation of these isomers is attended by considerable difficulty owing to the closeness of the boiling points. Thus, the α-halonaphthalenes prepared by halogenation of naphthalene can be freed from the β-isomers formed during the preparation (in amounts of up to 5-10%) only by repeated crystallization of the product from absolute ethanol or other solvents at a temperature of -15 to -20° [1-3]. Preparation of these aryl halides by Sandmeyer reaction, though it is a universal method, is distinguished by the considerable complexity of the preparation of the original amines and has a number of other disadvantages.

Now, aromatic hydroxy compounds such as naphthols, cresols, o-hydroxybiphenyl, and others are readily available industrial products, and a large number of them are stable crystalline substances, the purification and determination of the degree of purity of which are extremely simple. Therefore, a method proposed by British chemists [4] in 1957 for the preparation of aryl halides, ArX, from the corresponding hydroxy compounds, ArOH, and phosphorus pentachloride is of considerable interest. This method follows the following multistep scheme:

$$3Ar'OH + PCl_5 \xrightarrow{120-140^\circ} (Ar'O)_3PCl_2 + 3HCl;$$

$$(Ar'O)_3PCl_2 + ArOH \xrightarrow{120-140^\circ} (Ar'O)_3(ArO)PCl + HCl;$$

$$(Ar'O)_3(ArO)PCl \xrightarrow{250-350^\circ} ArCl + (Ar'O)_3PO,$$

where Ar'OH is an aromatic hydroxy compound possessing greater electron donor properties than does ArOH (phenol, p-cresol, or best of all, p-tert-butylphenol).

In the preparation of aryl bromides (ArBr) or aryl iodides (ArI), the $(Ar'O)_3(ArO)PCl$ is refluxed with excess C_2H_5Br or CH_3I before being pyrolyzed, for example:

$$(Ar'O)_3(ArO)PCl + C_2H_5Br \xrightarrow{t} (Ar'O)_3(ArO)PBr + C_2H_5Cl;$$

$$(Ar'O)_3(ArO)PBr \xrightarrow{250-350^\circ} ArBr + (Ar'O)_3PO.$$

However, in spite of the great electron donating power of the Ar'OH, some of the undesired halide Ar'X is always formed during pyrolysis of the reaction products under the conditions indicated:

$$(Ar'O)_3(ArO)PX \xrightarrow{250-350^\circ} Ar'X + (Ar'O)_2(ArO)PO.$$

Ar in the initial ArOH	ArCl						ArBr						
	yield, %	b.p. °C (mm)	m.p. °C	Cl content, %		literature data [6]	yield, %	b.p. °C (mm)	$n^{20}D$	d^{20}_4	Br content, %		Literature data [6, 7]
				found	calc.						found	calc.	
m-$CH_3C_6H_4$	–	–	–	–	–	–	70	180.5-182 (751)	1.5528	1.4106	46.98 46.87	46.72	B.p. 184-184.1° (754.1 mm); d^{20}_4 1.4099
α-$C_{10}H_7$	93•	112.5-113(4)	–	21.51 21.21	21.84	B.p. 262.7(760) $n^{20}D$ 1.6332; d^{20}_4 1.1938	87	140-140.5 (13)	1.6580	1.4830	38.64 38.62	38.60	B.p. 281.1° (760 mm); $n^{20}D$ 1.6582; d^{20}_4 1.4834
β-$C_{10}H_7$	92-95	263-265(760)	55-56	21.63 21.49	21.84	B.p. 121-122° (12 mm); m.p. 58°	93.5••	162-163.5 (8.5)	–	–	38.04 37.91	38.60	B.p. 281-282° (760 mm); m.p. 58-59°
o-$C_6H_5C_6H_4$	92.5	98-98.5(2.5)	31-32	19.06 19.27	18.83	B.p. 267-268° (760 mm) m.p. 34°	79	90-91.5 (1.5)	1.6243	1.2766	34.02 33.95	34.29	B.p. 160° (11 mm); d^{26} 1.2175

•$n^{20}D$ 1.6335; d^{20}_4 1.1937. ••M.p. 56.5-57° (from alcohol.)

and the yield of Ar'X reaches 70% when Ar' is C_6H_5 and 50-55% when Ar' is p-tert-$C_4H_9C_6H_4$. Thus, for example, even when Ar' is p-tert-$C_4H_9C_6H_4$, the yield of β-chloronaphthalene is 65%, that of its α-isomer is 60% [4], and, as we have shown, that of o-chlorobiphenyl is only about 50%.

Aryl bromides (ArBr) are formed in still lower yields, since, naturally enough, the exchange of bromine for chlorine in the compound $(Ar'O)_3(ArO)PCl$ is not quantitative, and the pyrolysis products contain four different halides (ArBr, ArCl, Ar'Br, and Ar'Cl). Of course, this not only decreases the yield of ArBr, but it also makes separation and purification of the ArBr difficult. Thus, while the yields of p-ClC_6H_4Cl from p-ClC_6H_4OH and of p-$CH_3C_6H_4Cl$ from p-$CH_3C_6H_4OH$ are 71 and 87%, respectively, the yields of the corresponding bromides are only 45 and 51% [4]. We were able to prepare o-bromobiphenyl with a yield of only 25-30% by this route (the yield of o-chlorobiphenyl was about 50%).

These disadvantages served to stimulate us to develop a modification of this method for the synthesis of individual aryl halides, ArX, starting with the corresponding hydroxy compound, ArOH, and PX_5. It was found that preparation of ArCl by replacement of the hydroxyl group in ArOH by chlorine can be carried out in a single stage by heating the appropriate aromatic hydroxy compound with phosphorus pentachloride (in a mole ratio of 4 : 1) at 140-160° for 3-5 hr with subsequent pyrolytic decomposition of the resulting tetraaryloxyphosphorus chloride at 280-300°.

$$4ArOH + PCl_5 \xrightarrow{140-160^\circ} (ArO)_4PCl + 4HCl;$$

$$(ArO)_4PCl \xrightarrow{280-300^\circ} ArCl + (ArO)_3PO.$$

Regardless of the electron donor capacity of the original ArOH, the yields of aryl chlorides by this method are almost theoretical (92-95%).

We also prepared a series of individual aryl bromides, ArBr, in a similar manner, starting with ArOH and PBr_5 (mole ratio of 4 : 1); the yields were 70-95% of theoretical:

$$4ArOH + PBr_5 \xrightarrow{130-140^\circ} (ArO)_4PBr + 4HBr;$$

$$(ArO)_4PBr \xrightarrow{250-260^\circ} ArBr + (ArO)_3PO.$$

This modification of the reaction allowed us to exclude completely the formation of contaminating by-product aryl halides, ArX; we were also able to shorten considerably (by a factor of 2-5) the duration of the process and to increase the yields of aryl halides by a factor of 1.5-2. The use of some excess ArOH over the stoichiometric amount did not decrease the yield of ArX and did not make purification of the latter more difficult, since the ArOH could readily be removed by treatment of the reaction products with a base. An advantage of this method is that the triarylphosphates, $(ArO)_3PO$, formed during the pyrolysis could be partially hydrolyzed (about two-thirds) by heating for 5-8 hr with a base, and the resulting hydroxy compounds could again be used for the preparation of aryl halides without any special purification. Hydrolysis of the mixed phosphates $(Ar'O)_2(ArO)PO$ or their mixture with $(Ar'O)_3PO$, all of which are formed under the conditions of reference [4], unfailingly leads to a difficultly separable mixture of two hydroxy compounds, Ar'OH and ArOH

Predried analytical grade naphthols were used in the preparation of the halonaphthalenes. The biphenyl was separated by 2- or 3-stage vacuum fractionation of the kettle residue from the production of phenol by the alkali fusion method (sometimes with subsequent recrystallization from petroleum ether); b.p. 89-91° (1 mm), m.p. 54-56°; literature m.p. [5], 58°. The phosphorus pentabromide was prepared immediately before an experiment by bromination of PBr_3 with bromine in an inert solvent ($CHCl_3$, CH_2Cl_2.)

Preparation of aryl chlorides. The reactants, 125 g (0.6 mole) of phosphorus pentachloride and 346 g (2.4 mole) of dry β-naphthol, were introduced under nitrogen into a flask fitted with a stirrer, a reflux condenser, and a thermometer. The mixture was stirred at 140-145° for 5 hr, and was then pyrolyzed at 300° for 15-20 min. Distillation of the products under vacuum yielded 92.5 g (95%) of β-chloronaphthalene with an m.p. of 55-56° (from 96% ethanol). A mixture of this material with a sample of β-chloronaphthalene prepared by isomerization of α-chloronaphthalene over silica–alumina catalyst melted without depression of the melting point. There was almost no change in the yield of β-chloronaphthalene (92%) when the heating time of the mixture of β-$C_{10}H_7OH$ and PCl_5 was shortened from 5 to 3 hr. α-Chloronaphthalene and o-chlorobiphenyl were prepared in an analogous manner.

Preparation of aryl bromides. To 49.5 ml (0.52 mole) of PBr_3 in 100 ml of $CHCl_3$ was added dropwise a solution of 27.7 ml (0.54 mole) of bromine in 100 ml of $CHCl_3$ (the temperature of the reaction mixture was maintained at -15 to -5°; the reaction mixture was stirred for 4.5 hr). To the resulting yellow precipitate of PBr_5 was added dropwise, at room temperature, 216 g (2 moles) of m-cresol; the addition required 2 hr. The solvent was then distilled, and the mixture was heated at 130° until the evolution of HBr ceased (2 hr). The mixture was then pyrolyzed at 280° for 30 min. The m-bromotoluene was separated by distillation of the pyrolysis products, and was treated with an aqueous solution of a base and again distilled. The yield was 59.5 g (70%). Synthesis of other aryl bromides was carried out in a similar manner, but with less reaction time.

The properties and elemental analyses of the aromatic chlorides and bromides prepared in the present work are presented in the table.

Hydrolysis of triarylphosphates. A mixture of 17 g (0.036 mole) of $(\beta\text{-}C_{10}H_7O)_3PO$ and 18.3 g (0.321 mole) of KOH in 50 ml of water was stirred at 100-105° for 5 hr, and the mixture was then treated with 150 ml of 10% HCl. The resulting white precipitate was separated by filtration, washed with water, and dissolved in 120 ml of ether. The ethereal solution was dried over Na_2SO_4, the ether was distilled, and the residue was distilled under vacuum. The β-naphthol obtained by this process amounted to 10 g (65% of theoretical); b.p. 141-143° (10 mm); m.p. 120-121°. A mixture of this material with a known sample of β-naphthol melted without depression of the melting point. A b.p. of 285-286° and an m.p. of 122° are reported in the literature [6].

Hydrolysis of $(\alpha\text{-}C_{10}H_7O)_3PO$ in a similar manner gave a yield of α-naphthol of 9.3 g (60%). According to data reported in reference [8], alkaline hydrolysis of $(C_6H_5O)_3PO$ under the influence of an excess of 1 N NaOH takes place to the extent of about two-thirds of that possible (the phenol yield was 63%).

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STRUCTURAL CORRESPONDENCE IN CATALYSIS

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The development of the theory of the selection of catalysts is a real problem in contemporary chemistry. The principles of structural and energetic correspondence between the catalyst and reacting molecules, which are important in this respect, follow from the multiplet theory of catalysis [1]. The first of these principles was established by the author in 1929 [2], when a table of metals arranged with respect to their crystal lattice type and atomic radii was presented as one of the proofs. In accordance with the sextet model of the multiplet theory, metals belonging to systems A1 and A3 with atomic radii within the range of 1.397 to 1.236 A were found to be catalysts of low-temperature (~ 300°) dehydrogenation of cyclohexane hydrocarbons (or the reverse reaction, namely, hydrogenation of benzene hydrocarbons). Up to now this table has remained unchanged, apart from the fact that in 1951 Trapnell [3] simplified and slightly augmented it. Long, Frazer, and Ott [4], Emmett and Skau [5], and Rienäcker and Unger [6] extended the same rule to alloys.

Over a period of time there have accumulated further proofs of the importance of structural factors in catalysis and, in particular, experimental results supporting the sextet model. A review of them was given by the authors in [7-10] and most recently in [11]. However, since two years have already elapsed since [11] was written, it is expedient to present even further data.

In 1958 there appeared a new, detailed summary of interatomic distances [12]. On the basis of this, it is possible to compile Table 1, which is presented below. Table 1 contains only metals and, moreover, only those that crystallize in the simplest systems A1, A2, A3, and A4. Metals which crystallize in more complex systems and even more so nonmetals that are the same in form, which are stable only at high temperatures (at which catalysts sinter), are not included in Table 1. Therefore, it does not include, for example, γ-U, A2, d = 3.058 A (805°C), β-Ti, A2, d = 2.8636 A (900°), γ-Fe, A1, d = 2.578 A (916°).

Table 1 shows that the rule found previously is retained completely with the new values of the interatomic distances. Precisely the elements that are cyclohexane dehydrogenation catalysts are actually only metals with lattices of types A1 and A3 and, moreover, those with the shortest interatomic distances $\underline{d}$, lying in the range of 2.7746 A (Pt) to 2.4916 A(Ni) (or, correspondingly, with atomic radii $R = d/2$ from 1.3873 to 1.2458 A, cf. above.) These elements are surrounded by a box in Table 1.

The boxes in Table 1 include rhenium, for which x-ray structural investigation and determination of the catalytic activity had not been carried out when the original table was compiled [2]. The multiplet theory predicts that Re dehydrogenates cyclohexane and this was demonstrated by the author, Karpeiskaya, and Tolstopyatova [13].

In a further study of catalysis over Re it was possible to find the case where so-called irreversible catalysis of cyclohexene (according to the terminology of N. D. Zelinskii) over Re proceeds more slowly than dehydrogenation of cyclohexane to benzene. As these cases do not differ in any way in principle from the dehydrogenation of cyclohexane over Pt and other similar metals, the contradictory sextet scheme proposed by some authors [14]

TABLE 1

Types of Crystal Lattice and Minimum Interatomic Distances d (in A)

Face-centered cubic lattice, A1	Body-centered cubic lattice, A2	Hexagonal lattice, A3	Diamond lattice, A4
α-Ca 3,947	Cs 5,309	β-Sr 4,32; 4,324	α-Sn 2,8099
Yb 3,880	Rb 4,95	α-La 3,739; 3,770	Ge 2,4498
γ-Ca 3,877	K 4,544	Nd 3,628; 3,658	Si 2,3517
Ac 3,756	Ba 4,347	Gd 3,573; 3,636	C 1,5445
β-La 3,745	γ-Sr 4,20	Y 3,551; 3,647	
Ce 3,650	Eu 3,989	Tb 3,525; 3,601	
α-Pr 3,649	Na 3,7157	Dy 3,503; 3,590	
α-Th 3,595	β-Tl 3,362	Ho 3,486; 3,577	
δ-Pu 3,279	ε-Pu 3,150	Er 3,468; 3,559	
Sc 3,212	Li 3,0390	Tu 3,447; 3,538	
Ag 2,8894	Ta 2,86	α-Te 3,4076; 3,4566	
Au 2,8841	Nb 2,8584	Lu 3,435; 3,503	
Al 2,8635	W 2,7409	α-Po 3,345	
Pt 2,7746	Mo 2,7251	Sc 3,256; 3,309	
Pd 2,7511	V 2,6224	Mg 3,1971; 3,2094	
Ir 2,714	Cr 2,4980	α-Zr 3,1790; 3,2313	
Rh 2,6901	α-Fe 2,4823	α-Hf 3,1275; 3,1947	
Cu 2,5560		Cd 2,9788; 3,2933	
Co 2,5061		α-Ti 2,8956; 2,9505	
Ni 2,4916		Re 2,741; 2,760	
		Tc 2,703; 2,735	
		Os 2,6754; 2,7354	
		Zn 2,6649; 2,9129	
		Ru 2,6502; 2,7058	
		α-Be 2,2260; 2,2856	

with the dehydrogenation of cyclohexane proceeding through irreversible catalysis (i.e., cyclohexene is first formed and this disproportionates to cyclohexane and cyclohexadiene with the latter giving benzene) is refuted.

It is interesting that according to Table 1, technetium is also included in the dehydrogenation catalysts. Therefore, theoretically one would expect catalytic dehydrogenation of cyclohexane rings over Tc. It is desirable to check this predication experimentally; due to the radioactivity of technetium, it will probably be difficult to investigate its catalytic properties.

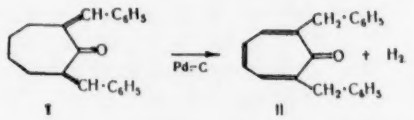
The question of whether Cu, which lies within a box in Table 1, is a catalyst of benzene hydrogenation has been the subject of discussion. The recent investigation of Erofeev and Nikiforova [15] by means of infrared spectrography demonstrated that Cu is actually a catalyst for this reaction as for the direct dehydrogenation of cyclohexane to benzene. This confirms the sextet model. The low activity of Cu in these reactions is explained by other, nonstructural factors (cf. [1]).

Manganese is not reduced to the metal from its oxides at temperatures below the beginning of sintering. Therefore, nothing is known of its capacity to dehydrogenate cyclohexane. Agronomov and Luzikov [16] recently prepared catalytically active, chemically pure metallic Mn by electrolysis. The low-temperature modification of Mn has a complex lattice (A12) and therefore it is not included in Table 1. In accordance with the theory, cyclohexane cannot be dehydrogenated over manganese [16].

The fact that a reduced iron catalyst is unable to produce hydrogenation of benzene and dehydrogenation of cyclohexane has been demonstrated by many investigators (see, for example, [4-6]). In actual fact, Fe lies outside the boxes in Table 1. Nonetheless, as Anderson and Kemball showed [7], Fe and W in the form of films condensed from vapor are found to be active in the hydrogenation of benzene. It should be pointed out, however, that the mechanism of reactions for reduced catalysts and for films are different, for example, in the chemisorption of N_2 on Fe. The rate of this process on reduced Fe is proportional to the N_2 pressure [18] and on Fe films it is proportional to the square root of the N_2 pressure [19]. Therefore, in the hydrogenation of benzene on Fe and W films there is apparently not a sextet (with a planar orientation of benzene), but another, slower mechanism, namely, a doublet mechanism (with edge orientation of the molecule). The latter has long been known for the dehydrogenation, for example, of ethane on Pd at high temperatures (cf. in the work of the author and Brusov [20]). Therefore, the data of Anderson and Kemball do not contradict Table 1.

The dehydrogenation mechanism examined here may be checked in a new way, namely, in the dehydrogenation of seven- and five-membered rings with the formation of nonbenzenoid aromatic compounds.

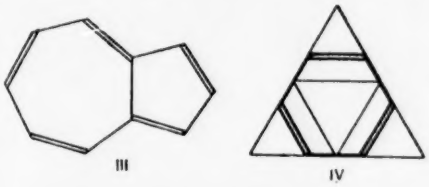
It was recently found [21] that over Pd, 2,7-dibenzylidenecycloheptanone (I) is isomerized and dehydrogenated at 290° in solution to give 16% of 2,7-dibenzyltropone (II), in which the seven-membered ring has an aromatic character.



I II

Analogs with substituents in the phenyl groups behave analogously to I. One molecule of H_2 is eliminated from I and consequently dehydrogenation proceeds by a doublet mechanism in this case (cf. above on the dehydrogenation of ethane over Pd). Incidentally, the migration of the double bond is also a doublet reaction, which is known for Pd.

An excellent demonstration of the sextet model is the fact that bicyclo-(0,3,5)-decane is dehydrogenated only in low yield over Pd [22] to azulene (III), which has aromatic properties. As in the case of I, the bulk of the material is decomposed and azulene is evidently formed by dehydrogenation by a doublet mechanism. Thus, though aromatic character affects catalysis in a definite way [23], in itself it is unable to lead to the smooth dehydrogenation which occurs in the case of cyclohexane. Structural correspondence is also necessary for catalysis to occur. Bicyclo-(0,3,5)-decane does not have common elements of symmetry with the Al lattice of palladium and cannot be superposed on it in accordance with the sextet model, while cyclohexane is fully capable of this (IV).



III IV

Table 1 of the present communication should replace the earlier, less accurate tables, i.e., the table in the article of the author [2] from 1929 and the table compiled by Trapnell [3] in 1951 on the basis of the former. It is understood that Table 1 may be applied not only to sextet, but to other catalytic reactions on metals, for example, the hydrogenation of olefins or aldehydes. In this case the optimal catalysts will be determined by other structural principles which also stem from the multiplet theory, in particular, the principle of retention of the valence angle [24]. The optimal catalyst for the doublet hydrogenation of a > C = C < bond is found to be Rh [25] (d = 2.6901 A), while the hydrogenation of the shorter > C = O bond should proceed best on Ru for which d is correspondingly less (d = 2.6502 A). Ruthenium is actually an excellent catalyst [26] for the hydrolytic hydrogenation of cellulose to sorbitol, which we proposed.

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SPECTRAL INVESTIGATION OF THE CONFORMATIONS OF CYCLOHEXANONE AND SOME OF ITS DERIVATIVES

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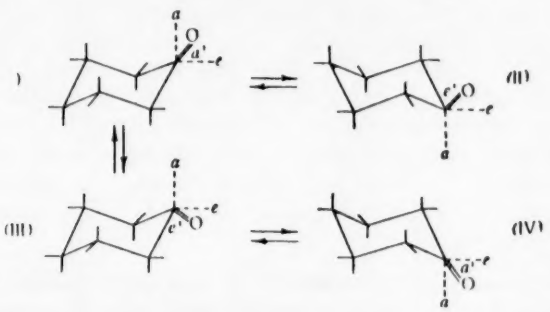
At room temperature, cyclohexanone, like cyclohexane [1], exists predominantly in the chair form, as follows from an electron-diffraction study of its structure [2]. In this study it was stated that the angle $\angle C_2C_1C_6$ is not equal to the angles $\angle OC_1C_2$ and $\angle OC_1C_6$; the first was found to equal 117 ± 3° and the other two, 121.5 ± ±1.5°. If each of these three angles equaled 120° or the sum of all three angles equaled 360°, then the carbonyl bond would be completely coplanar with the plane of atoms C_1, C_2, and C_6. However, the considerable range of error in the measurement of the angles gives grounds for considering that this coplanarity may be absent and the C = O bond may be somewhat displaced from the plane defined by the carbon atoms C_1, C_2, and C_6 either in an axial (quasiaxial direction a') or equatorial direction (quasiequatorial direction e'.) In this case it would be possible to consider the existence of four conformations of the chair form of cyclohexanone, but due to the equivalence of the C-H bonds, conformations (I) and (IV) should be regarded as identical, and likewise conformations (II) and (III), and, therefore, it would actually be possible to speak of two conformations of cyclohexanone, differing in the quasiaxial (a') and quasiequatorial (e') direction of the C = O bond:



This hypothesis is supported by spectral data: In the Raman spectrum of liquid cyclohexanone (and also a 12% solution of it in carbon tetrachloride) the frequency of the carbonyl group vibration and also that of ring pulsation are split into doublets [1706 (7) and 1719 (5) cm^{-1} and 748 (10) and 756 (8) cm^{-1}, respectively]; many other frequencies are also split into doublets or have the character of a double line. Judging by the intensities, one

of the conformations is present in a somewhat smaller amount (~40%) than the other (60%). What has been stated is confirmed by spectral investigation of the other compounds examined in this article.•

According to [3-5], α-chlorocyclohexanone exists in the preferred conformation with the C-Cl bond in the axial position (the so-called a conformation), as the conformation with this bond in the equatorial position (so-called e conformation) is found to be unstable due to the strong repulsion of the C = O and C - Cl dipoles when they are almost coplanar in the e conformation. According to data from infrared absorption spectra ([5] and also [3, 4]), the vibration frequency of the carbonyl group in the a conformation of α-chlorocyclohexanone is high (1722 cm^{-1}) as compared with cyclohexanone (1712 cm^{-1}) and is even higher in the e conformation (1740 cm^{-1}). The intensity of the latter frequency is low, indicating that the a conformation of α-chlorocyclohexanone is preferred.

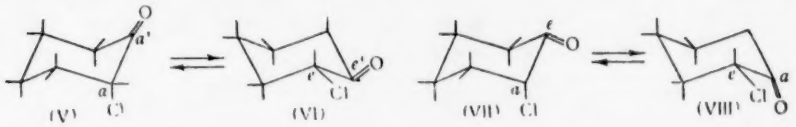
In recently published work [6], Kozima and Yamanouchi attempted to disprove Corey's hypothesis [5] that the a conformation of α-chlorocyclohexanone is preferred and suggested that the e conformation is preferred. However, this statement of theirs was contradicted by their own experimental data presented in [6]. Kozima and Yamanouchi came to their conclusion from certain general considerations on the basis of noncharacteristic vibration frequencies, the correct assignment of which is always either difficult or impossible. They completely avoided the extremely characteristic band of the carbonyl group, apparently because of the complexity of its contour (see [6], p. 4162). Meanwhile, according to the data they presented on the infrared absorption frequencies of the carbonyl group, there are two partly overlapping bands, which were reported by Corey in [5], with the same ratio of intensities in the liquid phase and in CS_2 and CCl_4 solutions: an extremely intense band at 1723 cm^{-1} and a weak one at 1743 cm^{-1}. In the gas phase, the center of gravity of these overlapping bands moved toward higher frequencies (maximum intensity at 1739 cm^{-1}) and in the solid state, toward lower frequencies (1723 cm^{-1}); in the solid phase, the second frequency (1743 cm^{-1}) was vanishingly low in intensity (see Table 1 on p.4160 in [6]). This means that the conformation characterized by the high vibration frequency of the carbonyl group of 1743 cm^{-1} is energetically more strained and unstable and predominates only in the gas phase at a higher temperature. With a fall in temperature and a change from the liquid to the solid phase, there should be "freezing out" of this unstable conformation; under these conditions the more stable conformation characterized by the carbonyl vibration frequency of 1723 cm^{-1} is retained and undoubtedly predominates. The unstable conformation with a carbonyl vibration frequency of 1743 cm^{-1} is the e conformation and the stable conformation with the carbonyl vibration frequency of 1723 cm^{-1} is the a conformation in view of the following circumstances. In aliphatic ketones, a halogen in the position α to the carbonyl always raises the vibration frequency of the latter (see, for example, [7]); the reaction of the C-Cl and C = O bonds and consequently the effect of the former in raising the vibration frequency of the latter is much greater with both bonds in the equatorial position [1, 8], i.e., in the e conformation and not in the a conformation in which the C - Cl bond is axial; hence it follows directly that the conformation with the carbonyl vibration frequency of 1723 cm^{-1} is the stable a conformation of α-chlorocyclohexanone, which predominates in the liquid and solid phases and also in solutions of this substance in CS_2 and CCl_4. The conformation with the higher carbonyl vibration frequency of 1743 cm^{-1} is the unstable e conformation, which predominates only in α-chlorocyclohexanone in the gas phase. These conclusions of ours from an analysis of the experimental data in [6] are in complete agreement with our data presented in the present article and the data of Corey in [5] and do not confirm the conclusions of Kozima and Yamanouchi in [6], which are contrary to fact. We should note that the Raman spectrum of α-chlorocyclohexanone presented in [6] is unsatisfactory; for example, in it the complex carbonyl band is represented by only one frequency (1721 cm^{-1}), when in actual fact four frequencies are observed in this region. Only two frequencies (2899 and 2949 cm^{-1}) are reported for the region of valence vibrations of C-H bonds in [6], when in actual fact there are thirteen frequencies in this region (including composite frequencies), etc.

The Raman spectrum (of α-chlorocyclohexanone) that we investigated confirmed the above hypothesis of Corey [5] on the preferred axial position of the C-Cl bond in the liquid phase of this substance and its solution in CCl_4 and also indicated the greater variety of conformations in which α-chlorocyclohexanone exists than was

• We should note that there are no grounds for attributing the splitting of the vibration frequency of the C = O bond of cyclohexanone we observed to Fermi resonance; it occurs with monosubstituted cyclohexanones and cyclopentanone and its derivatives, for most of which there is not even a hint of the possibility of the appearance of Fermi resonance.

described in [5]. In actual fact, in the region of carbonyl group vibration frequencies there was an intense doublet at 1719 (7) and 1729 (5) and a weaker doublet at 1734 (2) and 1746 (2) cm^{-1}, i.e., not two, but four frequencies. According to the results of our previous investigations [1, 8] and what has been said above on cyclohexanone and α-chlorocyclohexanone (especially on the possibility of the quasiaxial (a') and quasiequatorial (e') positions of the carbonyl), it can be assumed that for the latter substance there are four possible conformations, the most preferred of which is the trans-1a'2a (V); together with (V), there is apparently a substantial amount of the cis-1e'2a conformation (VII) present; the conformations (VI) and (VIII) are also present in the equilibrium mixture, but in a considerably smaller amount:

(V) trans-1a'2a ⇌	(VI) trans 1e'2a	(VII) cis-1e'2a ⇌	(VIII) cis-1a'2e
C-Cl 539 (9)		552 (2)	533 (6)	544 (3)
C = O 1719 (7)		1734 (2)	1729 (5)	1746 (2)
Ring 713 (5)		722 (2)	694 (3)	705 (2)

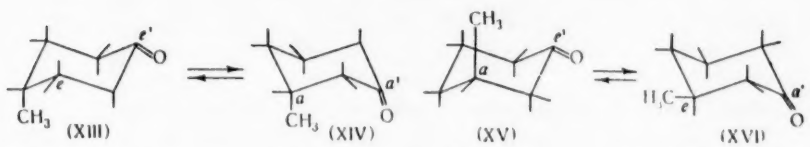


In the case of α- and more so with β-methylcyclohexanone, the factor is absent which causes the C-Cl bond in α-chlorocyclohexanone (strong repulsion of the C = O and C-Cl dipoles with the C-Cl bond in the equatorial position) to occupy the axial position preferentially, contrary to Hassel and Barton's rules. In these compounds, the methyl group mainly occupies the equatorial position in accordance with these rules [1, 8]. Therefore, in α-methylcyclohexanone the preferred conformation is the trans-1e'2e (IX); there is also present an appreciable amount of the cis-1e'2a conformation (XI) with the methyl group in the axial and the carbonyl group in the quasiequatorial position:

(IX) trans-1e'2e ⇌	(X) trans-1a'2a	(XI) cis-1e'2a ⇌	(XII) cis-1a'2e
C = O 1709 (8)		1695 (0)	1720 (5)	1703 (1)
Ring 721 (8)		716 (0)	727 (3)	733 (0)

In β-methylcyclohexanone the preferred conformations are the cis-1e'3e (XIII) and also trans-1a'3e (XVI) with the methyl group in them in equatorial positions:

(XIII) cis-1e'3e ⇌	(XIV) cis-1a'3a	(XV) trans-1e'3a	(XVI) trans-1a'3e
C = O 1708 (8)		1692 (0)	1700 (1)	1721 (6)
Ring 754 (8)		740 (0)	747 (1)	763 (6)



The Raman spectra were obtained on a Soviet ISP-51 spectrograph with a central camera and on a Hilger E612 spectrograph from the exciting blue line at 4358 A of a mercury lamp (see [1, 8] for the intensity symbols).

Physical Properties of Compounds Investigated (synthesis [9])

Compound	M. p., °C	B.p., °C/mm	$n^{20}D$	Compound	B.p., °C/mm	$n^{20}D$
Cyclohexanone	–	52 / 20	1.4507	α-Methylcyclohexanone	47 / 10	1.4480
α-Chlorocyclohexanone	23	57 / 3.5	1.4835	β-Methylcyclohexanone	56 / 15	1.4454

Cyclohexanone, $\Delta\nu$,cm^{-1}: 190 (1), 314 (3 d), 412 (6), 480 (1•), 492 (4 d), 655 (7 b,d), 748 (10•s). 756 (8•s), 783 (0) 842 (7), 895 (2• d), 910 (3• d), 995 (2), 1021 (9), 1057 (1•), 1075 (5• d), 1118 (5), 1224 (5), 1250 (4), 1268 (3), 1318 (6d), 1350 (2), 1422 (4•), 1431 (3•), 1451 (6••), 1463 (2••), 1706 (7•), 1719 (5•), 2668 (2••), 2686 (2••), 2827 (2•), 2861 (10• d), 2895 (7•s), 2906 (7•s), 2930 (5•s), 2941 (10•s), 2954 (10•s), 2967 (5•), 2980 (1•).

α-Chlorocyclohexanone, $\Delta\nu$ cm^{-1}: 200 (3 b), 235 (5), 261 (2), 312 (3), 335 (9), 409 (2•), 425 (3•), 533 (6••), 539 (9 s••), 544 (3 s••), 552 (2••), 659 (4•), 668 (4•), 694 (3••), 705 (2••), 713 (5•). 722 (2•), 756 (3), 800 (3), 824 (2•), 835 (3•), 842 (3•), 856 (4), 895 (3), 939 (2), 973 (7), 1022 (5•), 1032 (4•), 1071 (7), 1102 (2), 1128 (3 b), 1195 (4), 1230 (1•), 1249 (5•), 1266 (4•), 1302 (1••), 1316 (6••), 1335 (5), 1396 (1 b), 1424 (3•), 1434 (4•), 1454 (9••), 1467 (1••), 1719 (7•), 1729 (5•), 1734 (2•), 1746 (2•), 2643 (0••), 2662 (1••), 2687 (1••), 2810 (1), 2839 (1), 2870 (10•), 2901 (8•), 2914 (8•), 2919 (3•s), 2948 (10•), 2960 (10•), 2974 (7•), 2990 (2•).

α-Methylcyclohexanone, $\Delta\nu$,cm^{-1}: 242 (0), 290 (2), 327 (2), 394 (4), 427 (5), 504 (3), 576 (6), 632 (0), 662 (6 b d), 716 (0), 721 (8•s), 727 (3• s), 733 (0•), 840 (5), 868 (4), 966 (3), 993 (6 d), 1054 (3), 1070 (2), 1084 (2 d), 1121 (6 d), 1147 (4 d), 1164 (1), 1219 (4), 1239 (1), 1256 (6), 1286 (1), 1316 (7), 1347 (1•), 1361 (2•) 1432 (3••), 1454 (9••), 1467 (1••), 1695 (0), 1703 (1), 1709 (8•), 1720 (5•), 2653 (0••), 2671 (1••), 2690 (0••), 2732 (1 d), 2761 (0), 2807 (2•), 2827 (2•), 2854 (10•), 2869 (6•), 2930 (10•), 2942 (8•), 2965 (4•), 2982 (2•), 2995 (1•).

β-Methylcyclohexanone, $\Delta\nu$, cm^{-1}: 249 (1•), 266 (1•), 302 (1 b), 388 (3•), 399 (5•), 426 (0), 439 (3), 491 (3), 517 (3), 644 (8 b), 672 (1), 740 (0•), 747 (1• s), 754 (8• s), 763 (6• s), 786 (0), 822 (3•), 832 (3•), 864 (0••), 874 (1••), 890 (3), 948 (4), 963 (5•), 973 (4•), 1047 (5••), 1060 (1••), 1084 (7), 1109 (1), 1123 (8), 1207 (5), 1229 (7), 1266 (4•), 1276 (4•), 1306 (4••), 1319 (4••), 1328 (4••), 1339 (6••), 1361 (3), 1425 (6), 1460 (9), 1692 (0•), 1700 (1•), 1708 (8• s), 1721 (6• s), 2630 (0), 2652 (1•), 2679 (0•), 2716 (1••), 2737 (1••), 281 (3•), 2831 (3•), 2847 (4•), 2867 (10•), 2881 (3•), 2930 (6•), 2954 (10•), 2971 (5•).

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STABILITY OF COMPLEX COMPOUNDS OF DIVALENT PLATINUM

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The application of various physicochemical methods to the study of the stability of complex ions in solutions has made it possible to determine the instability constant for a very large number of compounds. Nonetheless, for the most typical complex formers, as are the platinum metals, the literature contains very few data on the instability constants. Even for such common and thoroughly studied compounds of divalent platinum as platinites $M_2[PtX_4]$, there are no data on the over-all instability constants.

Even in 1945, one of the authors of this article [1] gave a qualitative series in which anions were arranged with respect to their tendency to form complexes with the divalent platinum ion:

$$NO_3^- < SO_4^{2-} < Cl^- < Br^- < NO_2^-,\ SCN, I^- < CN^-.$$

By using data on the free energies of formation of ions, Latimer [2] calculated values for the over-all instability constants for chloro- and bromoplatinites:

$$\frac{[Pt^{2+}]\,[Cl^-]^4}{[PtCl_4^{2-}]} \approx 10^{-16}; \qquad \frac{[Pt^{2+}]\,[Br^-]^4}{[PtBr_4^{2-}]} \approx 3\cdot 10^{-21}.$$

Noting the similarity of these values to the experimental instability constants of the corresponding mercury compounds and extending this analogy to other platinites, one of the authors [3, 4] predicted the following approximate values for the over-all instability constants of iodo- and cyanoplatinites:

$$\frac{[Pt^{2+}]\,[I^-]^4}{[PtI_4^{2-}]} \approx 10^{-30}; \qquad \frac{[Pt^{2+}]\,[CN^-]^4}{[Pt\,(CN)_4^{2-}]} \approx 10^{-40}.$$

In the present work an attempt was made to obtain experimentally the over-all instability constants of chloro-, bromo-, iodo-, and cyanoplatinites.

EXPERIMENTAL

The concentration of Pt^{2+} ions in solution, which was required for calculating the over-all instability constants, was determined by measuring the emf of the cells:

$$\overset{+}{Pt}\,|\,\underset{C_1}{K_2[PtX_4]},\ \underset{C_2}{KX}\,\|\,KCl\ (\text{sat.}),\ Hg_2Cl\,|\,\overset{-}{Hg}$$

The measurement was carried out with a normal compensation circuit at a temperature of 18 ± 0.5°. The electrodes were made of platinum foil, 10 × 10 mm in size, and before an experiment they were platinized in a solution of chloroplatinic acid. The measurements were carried out in a nitrogen atmosphere to prevent passivation of the electrodes. The salt bridge connecting the solution investigated to the saturated calomel electrode was filled with 1 N KNO_3 solution. The measurements were made with a constant ionic strength $\mu = 1$, which was maintained by the addition of the required amount of $NaNO_3$ to the solution examined.

TABLE 1

Determination of Instability Constant of $[PtCl_4]^{2-}$

$K_2[PtCl_4]$ conc. (mole/liter)	KCl conc. (mole/liter)	$E = E_{Pt} - E_{cal}$ (mv)	E_{Pt} (mv)	$-\lg[Pt^{++}]$	pK^c
0,0041	1,0	418	666	18,4	16,0
0,0083	1,0	428	676	18,1	16,0
0,0042	0,5	417	665	18,4	17,2
0,0096	0,5	435	683	17,8	17,0
0,0183	0,5	434	682	17,8	17,2
0,101	0,5	459	707	17,0	17,2
0,0009	0,2	475	723	16,4	16,2
0,0132	0,2	503	751	15,5	16,4
0,0009	0,1	494	742	15,8	16,8

$pK^c = 16,6 \pm 0,6$

TABLE 2

Determination of Instability Constant of $[PtBr_4]^{2-}$

$K_2[PtBr_4]$ conc. (mole/liter)	KBr conc. (mole/liter)	$E = E_{Pt} - E_{cal}$ (mv)	E_{Pt} (mv)	$-\lg[Pt^{++}]$	pK^c
0,0037	1,0	313	561	22,0	19,6
0,0085	1,0	295	543	22,7	20,6
0,0677	1,0	303	551	22,4	21,2
0,0020	0,5	332	580	21,4	19,9
0,0040	0,5	323	571	21,7	20,5
0,0055	0,5	325	573	21,6	20,5
0,0040	0,2	370	618	20,0	20,4
0,0027	0,2	370	618	20,0	20,2
0,0680	0,2	407	655	18,8	20,4
0,0006	0,1	380	628	19,7	20,5
0,0011	0,1	410	658	18,7	19,7
0,0054	0,1	388	636	19,4	21,1

$pK^c = 20,4 \pm 0,8$

TABLE 3

Determination of Instability Constant of $[PtI_4]^{2-}$

$K_2[PtI_4]$ conc. (mole/liter)	KI conc., mole per liter: starting	KI conc., mole per liter: equil.	$E = E_{Pt} - E_{cal}$ (mv)	E_{Pt} (mv)	$-\lg[Pt^{++}]$	pK^c
0,0066	1,0	0,98	33	281	31,7	29,6
0,0098	1,0	0,96	21	269	32,1	30,1
0,096	1,0	0,62	77	325	30,2	30,0
0,0023	0,5	0,49	63	311	30,7	29,3
0,0082	0,5	0,47	56	304	30,9	30,1
0,0104	0,5	0,46	64	312	30,6	30,0
0,0563	0,5	0,28	108	356	29,1	30,0
0,0153	0,5	0,45	101	349	29,4	29,0
0,0019	0,2	0,19	87	335	29,8	30,0
0,0111	0,2	0,16	130	378	28,3	29,5
0,0008	0,1	0,1	104	352	29,3	30,2
0,0068	0,1	0,07	160	408	27,3	29,7

$pK^c = 29,6 \pm 0,6$

TABLE 4

Determination of Instability Constant of $[Pt(CN)_4]^{2-}$

$K_2[Pt(CN)_4]$ conc. (mole per liter)	KCN conc. (mole/liter)	$E = E_{Pt} - E_{cal}$ (mv)	E_{Pt} (mv)	$-\lg[Pt^{++}]$	pK^c
0,0012	0,1	−184	64	39,1	40,2
0,0024	0,1	−186	62	39,2	40,6
0,085	0,1	−149	99	38,0	40,9
0,0006	0,05	−156	92	38,2	40,2
0,0012	0,05	−146	102	37,9	40,2
0,001	0,02	−135	113	37,4	41,2
0,0062	0,02	−128	120	37,2	41,8
0,0742	0,02	−91	157	36,0	41,7
0,0011	0,01	−72	176	35,3	40,3
0,0007	0,01	−117	131	36,8	41,7
0,0027	0,01	−98	150	36,2	41,6
0,0054	0,01	−93	155	36,0	41,7

$pK^c = 41,0 \pm 0,8$

Potassium chloroplatinite was obtained by the method of Gil'dengershel' and Shagisultanova [5] by reduction of potassium chloroplatinate with hydrazine sulfate. For the preparation of potassium bromoplatinite, a solution of potassium chloroplatinite was evaporated to small volume with hydrobromic acid in a stream of CO_2 [6]. Potassium iodoplatinite was prepared in solution by the addition of a definite amount of chloroplatinite to a hot solution of potassium iodide.

The cyanoplatinite was obtained by addition of chloroplatinite to a hot solution of potassium cyanide with subsequent crystallization from a concentrated solution. The composition of all the compounds was confirmed by chemical analysis.

A definite concentration of Cl^-, Br^-, I^-, and CN^- ions in solution was created by dissolving the salts KCl, KBr, KI, and KCN in water. All salts were purified by recrystallization. The emf was measured with time from the moment of solution of the complex until the potential was established. The experimental data are given in Tables 1-4.

The tables give the emf values after equilibrium had been established. In the case of cyanoplatinite, the emf slowly increased after equilibrium had been established, apparently due to decomposition of cyanide; equilibrium was considered established when the increase was not more than 0.5 mv/hr.

The equilibrium values of the emf were used to calculate the potential of the platinum electrode E_{Pt}. The potential of a saturated calomel electrode was taken as equal to 0.248 v. The value of the negative logarithm of the concentration of Pt^{2+} ions was found from the Nernst equation. The value of the normal potential $E^0_{Pt^{2+}/Pt}$ required for the calculation was taken as 1.2 v according to Latimer's data [2].

From the equilibrium concentrations $[Pt^{2+}]$, $[X^-]$, and $[PtX_4^{2-}]$ we calculated the negative logarithms of the concentration instability constants pK^C. In the case of iodoplatinite, the starting concentration of KI was corrected for the amount of KI consumed in the formation of iodoplatinite.

DISCUSSION OF RESULTS

An examination of the experimental data presented in Tables 1-4 shows that the values obtained for the over-all instability constants of chloro- and bromoplatinites agree well with the calculated data of Latimer. The over-all instability constants of iodo- and cyanoplatinites were close to the values predicted by one of the authors from the analogy with mercury complexes.

This agreement between the experimental and theoretical data indicate that the platinum electrode, which is widely used as an indifferent electrode due to its passivity, may be used as an electrode of the first order with respect to divalent platinum ions under the given conditions. As regards the mechanism whereby the potential is established, it seems very improbable that in the almost complete absence of free Pt^{2+} ions, they could play a substantial role in the establishment of equilibrium. The jump in potential apparently arises as a result of interaction of complex ions with the electrode. The mechanism of this interaction is still unclear. It is possible that an essential role in this interaction is played by processes of the V. M.* type $[PtX_4]^{2-} + 2e \rightleftharpoons [Pt^0X_4]^{4-} \rightleftharpoons Pt^0 + 4X^-$.

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COPOLYMERIZATION OF ETHYLENE WITH PROPYLENE AND α-BUTYLENE ON A CHROMIUM OXIDE CATALYST

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Copolymers from monoolefins are valuable as elastomers and plastics.

D. Natta [1] synthesized copolymers of ethylene and propylene on organometallic catalysts in the presence of heavy metal (titanium or vanadium) chlorides. A copolymer containing 50% of ethylene and 50% of propylene was superior in elasticity to butadiene–styrene rubber and approached natural rubber. A. Clark, J. Hogan, R. Banks, and W. Lanning [2] studied the copolymerization of ethylene with propylene, α-butylene, and other α-olefins on a chromium oxide catalyst. The copolymer obtained from a gas mixture of 10 weight percent propylene and 90 weight percent ethylene had a molecular weight and melting point which were lower than those of polyethylene synthesized under the same conditions. In their work Clark et al. presented a graph of copolymer molecular weight against reaction temperature. It was reported that the copolymer of ethylene and propylene was more flexible than polyethylene. The authors did not report other properties. Considering the importance of copolymers as elastic plastics, we undertook to synthesize copolymers of ethylene with propylene and α-butylene and study their properties in more detail. In the present article we present the first results of this work.

The copolymerizations were carried out in a Vishnevskii glandless mixer with a capacity of 2000 ml. The solvent used was extraction ligroin, which was first subjected to contact purification with an activated chromium catalyst. In all experiments the amount of solvent was 1000 g, the amount of catalyst, 5-6 g, and the amount of calcium carbide, 1 g.

The catalyst was prepared by a known procedure [4] by impregnation of the carrier with chromium trioxide and activation with air at 550°. The carrier used for the chromium catalyst was industrial aluminosilicate, containing approximately 90% SiO_2, 7-8% Al_2O_3, and small amounts of Fe, Ca, and Mg oxides. The pore volume of the aluminosilicate was 62% and the specific surface 220-350 m^2/g. The ethylene and propylene fractions of "Pyrogas" were used as monomers. The composition of the ethylene fraction in volume percents was: ethylene 99.2-99.6, methane 0.1-0.2, ethane 0.3-0.4, carbon monoxide 0.0050, and oxygen up to 0.0005. Sulfur compounds and carbon dioxide were practically absent. The moisture content of the gas did not exceed 10 mg/m^3.

The composition of the propylene fraction of Pyrogas in volume percents was: propylene 90, propane 8, ethane 0.7-1, C_4 hydrocarbons about 0.1, and dienes up to 0.03. The amount of sulfur compounds did not exceed 1 mg/m^3.

Butylenes were obtained by dehydration of n-butyl alcohol over A-1 grade alumina at 360°. The mixture contained 2-3% isobutylene and 97-98% normal butylenes. According to literature data [5], a mixture of butylenes obtained under the given conditions contains 75% of 1-butene and 22-23% of 2-butene.

During the preparation process, the butylene fraction was dried over finely porous silica gel and calcium hydride. The amount of residual moisture in the butylenes was not determined.

Properties of Polyethylene and Copolymers of Ethylene with Propylene and α-Butylene

Material	Characteristic viscosity (decalin, 135°C)	M.p., °C	Solubility in boiling n-heptane, %	Mechanical properties	
				$\frac{\Delta l}{l}$, %	P, kg/cm²
Polyethylene	1.8	127-130	10	300-490	250-300
Ethylene–propylene copolymer	1.5	120-122	65	700-1000	190-220
Ethylene–α-butylene copolymer	1.7	124-126	40	500-800	250-290

•$\Delta l/l$ is the relative elongation in cold stretching and P is the tensile strength.

The gas mixtures were prepared in carefully dried metal tanks. Experiments were normally continued until the fall in pressure in the autoclave ceased. The autoclave was then cooled, the pressure released, and the copolymer removed. The copolymer with the catalyst was heated in a vessel with ligroin and then filtered free from catalyst on a paper filter. The polymer was then washed with ethanol, dried, and analyzed.

Table 1 gives the properties of polyethylene, an ethylene–propylene copolymer containing 12.6 weight percent of propylene and 87.4 weight percent of ethylene, and an ethylene–α-butylene copolymer containing 7% butylene and 93% ethylene. All the samples were prepared at 110° and 49 atm.

As Table 1 shows, the copolymers of ethylene with propylene and α-butylene differed from polyethylene in melting point, solubility in n-heptane, and also relative elongation under cold stretch.

It is noteworthy that the ethylene–propylene copolymer was more flexible, but weaker than polyethylene. The ethylene–α-butylene copolymer approached polyethylene in strength, but was more flexible.

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PRESSURE OF SATURATED VAPOR OF LIQUID ANTIMONY AND ITS ASSOCIATION STATE

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The saturation vapor pressure of solid antimony was determined by Niwa and Yosiama [1] and then by Nesmeyanov and Iofa [2]. Investigations with liquid antimony have been described in a series of papers [3-8], but the authors of only the first three presented their own experimental data.

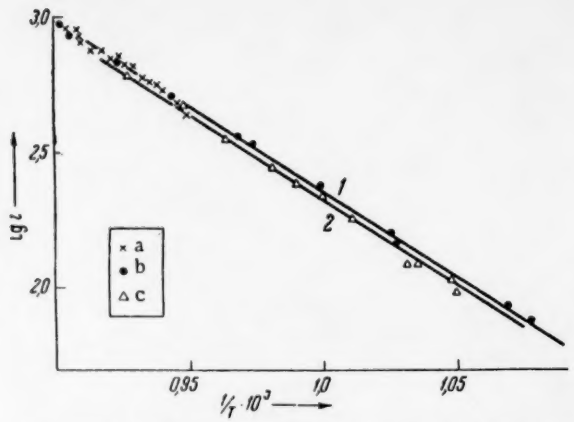
In calculations of vapor pressures in [1, 2, 5] it was assumed that the vapor consists of Sb_4 molecules and has a constant molecular composition over the whole region investigated, which some authors consider demonstrated by the linear relation between log P and 1/T. However, this relation is not a conclusive criterion of the absence of dissociation in saturated vapor. An example is the behavior of saturated selenium vapor, the association states of which change with temperature while the given linear relation is maintained [9, 10]. It is readily shown that the linear relation is maintained when the heats of evaporation and dissociation are equal or when the vapor pressures of the pseudocomponents are equal, if equilibrium between them is established in both phases.

Antimony vapor is considerably dissociated at high temperatures [11] and Eucken [12] considered that in this region there must be distortion of the relation examined as only in this case could the data in [4] be in accordance with the accurately determined boiling point [13].

We proposed a radiometric method for determining the density of vapor, which may be used when γ-radioactive isotopes are available. It is similar to the method of Dainton and Kimberley [14], which was used for determining the vapor pressure of white phosphorus. We determined the density of antimony vapor by this method.

Two vessels were placed in furnaces, one of which was thermostatted at a given temperature T_1, while the second, which contained the vessel with the substance investigated, was at a variable temperature T_2. This temperature was always below T_1 and lay within the region of the saturated vapor pressure. The vessels were connected by a heated capillary whose cross section was such that when equilibrium was established there was no appreciable pressure drop when the vessels were at different temperatures, produced by the Knudsen effect. If the vapor pressure curve and also the temperature and volume of the vessel in the first furnace are known, then the density of the vapor in it may be established remotely by radiometric determination of the mass. Vapor density isotherms are readily measured in this way. With the second furnace thermostatted and the temperature in the first varied continuously, the measurements are made isobarically.

In work with a previously given mass, it is necessary to maintain conditions corresponding to a saturated vapor state in both furnaces and to measure the activity in the vessels simultaneously. One of the vessels must be at a constant temperature corresponding to practically complete association or dissociation. In this case, the pressure may be determined by the fall in temperature in one of the vessels to the saturated state, which is observed as a sharp increase in radioactivity.



1) T_1 = 950°, a) upward plot, b) downward plot. 2) T_1 - 900°, c) upward plot. With allowance for decays and conversion to the same value of T_1, the lines coincided.

The investigations were carried out by the first variant. The furnaces used in the work were similar to the large furnace described previously [10, 15] and were placed in lead chambers with walls 2 cm thick. The volume of the quartz vessel in the first furnace was 55.973 ml. The volume of the part of the capillary whose radiation entered the counter was 1.119 ml. The temperature was measured with calibrated platinum–platinorhodium thermocouples by the compensation method with an accuracy of ± 1°. In each of the furnaces, measurements were made at six points by moving the thermocouples through jackets sealed inside the vessels and on the capillary in a quartz jacket. The capillary and jacket were bound together with a platinum heating wire and well insulated thermally. The axial temperature drop in the furnace from the center to the end did not exceed 2°. The temperature on the capillary during the whole of an experiment (up to 30 hr was required for taking a series of readings) was 1000 ± 10°. The furnaces were separated from each other so that radiation from the vessel in the second did not enter the counter set in front of the hinged door of the chamber opposite the opening, which corresponded accurately to the position of the vessel in the first furnace. The counter was placed in a thermostat with a fixed hollow tube to prevent a change in the γ-ray intensity from a thick layer of water.

Radioactive antimony was diluted with twenty times the amount of spectrally pure antimony, containing $1 \cdot 10^{-5}$% of impurity, and after five sublimations in high vacuum, it was distilled into the vessel in the second furnace. After the distillation, the high vacuum line was sealed off. The total activity of the charge was 2 mC.

We carried out one preliminary and three main series of experiments with the first furnace at 900 and 950°. The radiometric measurements were carried out both with the temperature being raised and being lowered. The points agreed with each other well. The radioactivity readings required five minutes each.

The results obtained are given in Fig. 1 as a plot of log $\underline{i}$ against $1/T$. They refer to experiments 2 (T_1 = = 950°) and 4 (T_1 = 900°). The points lie well on straight lines with the same isotope.

If log P is a linear function of $1/T$ it is possible to write

$$\log i = -\frac{\lambda}{4{,}576}T + \text{const} + \log\frac{A}{KR} + \log\frac{V\nu}{T_1} = -\frac{\lambda}{4{,}576}T + \text{const}' + \log\nu,$$

where $\underline{i}$ is the activity, K is the factor for conversion to mass, A is the atomic weight, V is the volume of the vessel, T_1 is the constant temperature in the first furnace, R is the gas constant expressed in appropriate units, and ν is the over-all degree of association.•

• The formula we used is accurate only when T_1 and the temperature in the capillary (T_3) are equal. When they are different, the term log $V\nu/T_1$ must be replaced by log $(T_3V_1\nu_1 + T_1V_3\nu)$: T_1T_3. We neglected this refinement as we considered that the correction thus introduced was low.

In a dissociation of the type $A_2 \rightleftharpoons 2A$, $\nu = 2 : (1 + X)$, where X is the degree of dissociation. According to the Law of Mass Action $X = [K_p : (4P + K_p)]^{1/2}$. Hence it follows that when $K \gg 4P$ and $K_p \ll 4P$, ν depends linearly on $1/T$. In the intermediate region there is a curvilinear dependence, except in those cases when ν may be expressed as a power function of P. Then log ν is related linearly to log P and consequently, to $1/T$. This leads to maintenance of the linear dependence of log i on the reciprocal temperature over the whole pressure range, but there is a change in the slope, as we observed in work with selenium.

When all the experiments were complete, part of the antimony was distilled into the vessel in the first furnace, the capillary sealed off in a position at which radiation did not enter the counter, and the standard radioactivity established at 950°. The cooled vessel was then opened and the antimony dissolved by Czervek's method [16]. After dilution of the solution, the activity of a portion was determined in a lead castle. This activity was compared with that of a solution prepared by the same method from an accurately weighed sample of antimony taken from the vessel in the second furnace. The antimony sample weighed 31.84 mg ± 9.12%. With corrections for decay up to the day of the last analyses, 1000 counts in our experiments corresponded to 1.8795 ± 0.0218 mg of antimony.

The measurements of all the experiments were converted to activities on the day on which the standard radioactivity was established. The results were expressed as formulas for the linear relation of log m to reciprocal temperatures, obtained by the method of least squares.

When the data from experiments at 900 and 950° were converted to one temperature, absolute agreement was obtained and this could only occur if the values of ν were identical at these temperatures. It is only possible to have identical values of ν at two different temperatures if there is no dissociation. This demonstrates unequivocally that unsaturated and consequently, saturated antimony vapor consists practically solely of Sb_4 molecules at temperatures up to 1000°.

The relations of log m to $1/T$ obtained were converted to relations of log P to the reciprocal temperature. The mean value for the three series gave

$$\log P = -\frac{6403{,}35}{T} + 6{,}1938.$$

According to this equation, the latent heat of evaporation equals 29.30 ± 0.60 kcal. This value differs from the value determined in [5] by 2.37 kcal. The latent heat of fusion, as the difference between the latent heats of evaporation and sublimation, equals 14.88 ± 0.60 and 19.79 ± 0.60 kcal according to the equations in [1] and [2], respectively. The latter value agrees well with reliable literature data, namely, 19.08 kcal per mole of Sb_4 [17]. Extrapolation to the triple point gives the value of 0.1278 mm. From the equations in [1] and [2] and also the equation which we derived from the data in [5], we obtain 0.1347, 0.2602, and 0.1772.

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CATALYTIC CONVERSIONS OF CYCLOOCTANE IN THE PRESENCE OF PLATINIZED CHARCOAL

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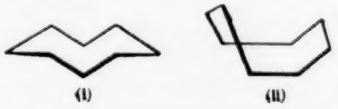
In their investigations of the manifestation of the transannular effect by polymethylenes with a medium sized ring under catalytic dehydrogenation conditions (5% Pd on charcoal at 400°), Prelog and his co-workers observed the conversions of C_9-C_{18} hydrocarbons [1]. Depending on the number of carbon atoms in the ring, with the elimination of hydrogen they obtain various polycyclic–aromatic and pseudoaromatic–hydrocarbons (indene, azulene, naphthalene, fluorene, phenanthrene, etc., right up to triphenylene.)

In view of the fact that platinum is a more active dehydrocyclization catalyst than palladium [2] and that in a number of cases in the presence of platinum it is possible to obtain in addition dehydrocyclization products of a nonaromatic character, we decided to see how polymethylenes with an average ring would behave in the presence of platinized charcoal at lower temperatures than those used in the work of Prelog. It also seemed interesting to repeat the essentially incomplete work of N D. Zelinskii and G. M. Freiman [3] in which they came to the conclusion that at 300° and in the presence of platinized charcoal, cyclooctane yields bicyclo-(0, 3, 3)-octane and methylcycloheptane, though they gave no experimental confirmation of this reaction course. As noted above, cyclooctane was not used as a subject for investigation in the work of Prelog.

According to contemporary ideas on conformation, cyclooctane may exist largely in the two most stable forms: the "crown" (I) and "boat" (II) forms [4]:

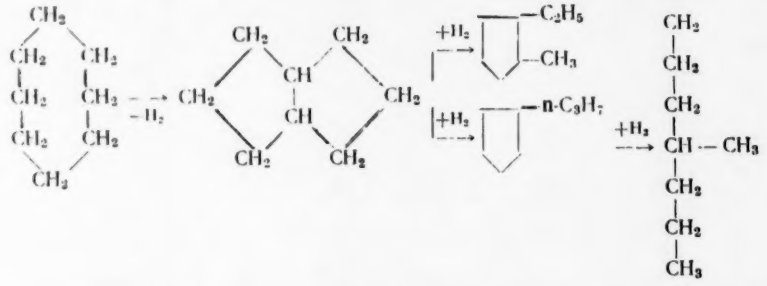


(I) (II)

The latter is apparently much less favored energetically than the former and therefore its relative content in cyclooctane should be very low. In the centrosymmetrical form (I), four equatorial hydrogens lie above the mean plane of the ring and four below it; they approach very close to each other as is readily seen from a Brigleb–Stuart model. With the elimination of any pair of them in a 1,5 position, there is the possibility of the creation of a transannular C-C bond with the formation of cis-bicyclo-(0,3,3)-octane (cis-pentalane.)

In the present work we investigated the conversions of cyclooctane over platinized charcoal at 310° in the absence and presence of hydrogen. In both cases there was quantitative conversion of cyclooctane. In the absence of hydrogen, the main product was cis-bicyclo-(0,3,3)-octane (cis-pentalane) and this formed ~ 51% of the catalyzate weight. We also found appreciable amounts of trans-1-methyl-2-ethylcyclopentane (~ 23%) and n-propylcyclopentane (~ 20%); 4-methylheptane was formed in a smaller amount (~6%) and a very small amount

of aromatic hydrocarbons was also detected in the catalyzate. These products from the reaction give grounds for assuming that it proceeds according to the following scheme:



Thus, the first stage is apparently the formation of cis-pentalane, which then undergoes hydrogenolysis due to the hydrogen liberated during its formation to give trans-1-methyl-2-ethylcyclopentane and n-propylcyclopentane; hydrogenolysis of the latter leads to 4-methylheptane.

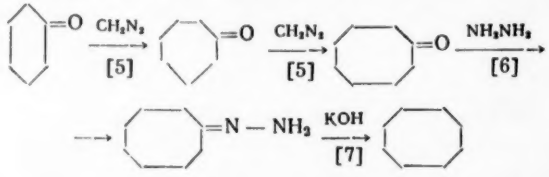
The same substances were obtained in the presence of hydrogen, but in different ratios: cis-pentalane only ~ 6%, trans-1-methyl-2-ethylcyclopentane ~ 15%, cis-1-methyl-2-ethylcyclopentane ~ 37%, n-propylcyclopentane only 2-3%. These ratios are explained by the fact that hydrogenolysis of the five-membered ring naturally proceeds much more rapidly in the presence of hydrogen, while pentalane and n-propylcyclopentane undergo hydrogenolysis more readily than 1-methyl-2-ethylcyclopentane. This is confirmed by the fact that the catalyzate contained a considerable amount of 4-methylheptane (~33%), the hydrogenolysis product from n-propylcyclopentane. Methylcycloheptane, which was reported by N. D. Zelinskii and G. M. Freiman, was not found among the reaction products.

A small amount (~ 1-2%) of aromatic hydrocarbons (toluene, ethylbenzene, and o-xylene) was also formed.

All the hydrocarbons listed above were identified largely by an examination of the Raman spectra of fractions obtained by distilling the catalyzate on an efficient column. The aromatic hydrocarbons were isolated by chromatography on silica gel.

EXPERIMENTAL

The cyclooctane used in the present work was obtained according to the following scheme:



and had the constants: b.p. 149.5°/745 mm; $n^{20}D$ 1.4592; d^{20}_4 0.8369. Literature data [8]: b.p. 150.70/760 mm; $n^{20}D$ 1.45851; d^{20}_4 0.8362.

Catalytic conversions of cyclooctane without carrier gas. A quartz tube was packed with 63 ml (16.6 g) of 5% platinized charcoal, which was prepared by the method of N. D. Zelinskii [2] and had a high activity in the dehydrogenization of cyclohexane. Over the catalyst was passed 44.5 g (0.4 mole) of cyclooctane at 310° and a space velocity of 0.2. The experimental results are given below:

Pass	$n^{20}D$	Amt. of gas evolved, ml	Catalyzate wt., g
1	1.4435	5883	40.74
2	1.4435	850	38.18
Total	–	6733	38.18

TABLE 1

Fraction No.	Boiling range at 745 mm	n_D^{20}	d_4^{20}	Amount, g
1	114—120	1,4173	0,7541	2,78
2	120—125,5	1,4216	0,7689	7,03
3	125,5—129,5	1,4260	0,7776	2,30
4	129,5—132	1,4334	0,7952	2,23
5	132—134,5	1,4431	0,8220	3,08
6	134,5—135,5	1,4538	0,8495	6,10
7	135,5—136	1,4595	0,8635	4,35
8	Residue	1,4603	0,8608	6,00
	Total	—	—	33,87

TABLE 2

Hydrocarbons present in fractions	Fraction No.								Total in catalyzate	
	1	2	3	4	5	6	7	8		
	hydrocarbon content, wt. %								g	wt. %
4-Methylheptane	20	20	5	—	—	—	—	—	2	6
n-Propylcyclopentane	—	10	40	65	50	30	10	—	7	20
Trans-1-methyl-2-ethylcyclopentane	70	60	40	10	—	—	—	—	8	23
Cis-bicyclo-(0,3,3)-octane	7	10	15	25	Main content of fraction				17	53

TABLE 3

Fraction No.	Boiling range at 736 mm	n_D^{20}	d_4^{20}	W., g	Wt. %
1	98,5—113,9	1,4110	0,7336	1,10	7,9
2	114,0—118,5	1,4072	0,7227	3,32	23,8
3	118,5—121,5	1,4120	0,7435	5,37	38,6
4	121,5—126,5	1,4189	0,7602	2,20	15,8
5	Residue	1,4412	0,7995	1,92	13,8

The gaseous products were analyzed on a VTI apparatus. Analysis results: H_2 99.4%; C_nH_{2n+2} 0.6%.

Investigation of catalyzate. For separation of the paraffin—naphthene hydrocarbons from the aromatics (the presence of which was detected by the formalite reaction), the catalyzate was chromatographed on silica gel and then fractionated on a column with an efficiency of 60 theoretical plates. The results of the distillation are given in Table 1.

The aromatic part of the catalyzate, which had $n^{20}D$ 1.4920, could not be investigated due to the very small amount (less than 0.1 g). The composition of fractions 1-8 was established by a study of their Raman spectra. The results of the spectral investigation are given in Table 2.

Catalytic conversions of cyclooctane in the presence of hydrogen. The experiments were carried out under conditions analogous to those described above. We used 20.7 g of cyclooctane for catalysis. The experimental results are given below.

Pass	$n^{20}D$	Catalyzate amt., g
1	1.4260	14.80
2	1.4150	13.91

TABLE 4

Hydrocarbons present in fractions	Fraction No.				Total in catalyzate	
	1+2	3	4	5		
	hydrocarbon content, wt. %				g	wt. %
4-Methylheptane	70	30	—	—	4,5	33
n-Propylcyclopentane	—	—	—	20	0,4	3
Trans-1-methyl-2-ethylcyclopentane	10	70	40	—	5,1	37
Cis-1-methyl-2-ethylcyclopentane	—	+	50	50	2,1	15
Cis-bicyclo-(0,3,3)-octane	—	—	+	20	0,4	3
Toluene	2	—	—	—	0,08	0,6
Ethylbenzene	—	—	2	+	0,04	0,3
o-Xylene	—	—	+	10	0,19	1,4

Investigation of catalyzate. The catalyzate (13.9 g) was fractionated on a column with an efficiency of 60 theoretical plates. The distillation results are given in Table 3.

The composition of all the fractions was established by studying their Raman spectra. The results of the spectral investigation are presented in Table 4.

The procedure for obtaining and measuring the Raman spectra used in the present work was described in detail in the monograph of G. S. Landsberg, B. A. Kazanskii, et al. [9]. The intensity of the lines was estimated visually. Most of the spectra of individual hydrocarbons used to analyze the composition of the fractions were taken from the same monograph. The spectra of the cis and trans isomers of 1-methyl-2-ethylcyclopentane were taken from the work of B. A. Kazanskii, A. L. Liberman, et al. [10] and the spectrum of cis-pentalane, from the work of the same authors [11]. The relative content of components in each fraction was estimated by visual comparison of the intensities of the spectral lines.

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• See C. B. translation.

REACTION OF DIISPROPYLIDENEGLUCOSE WITH HALOGEN COMPLEXES OF TRIPHENYL PHOSPHITE

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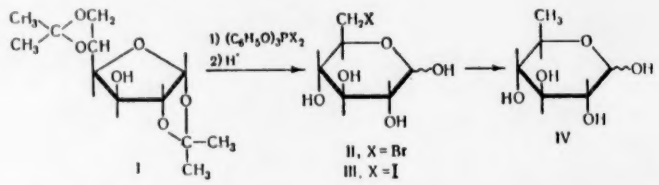
The extremely limited possibilities of synthetic conversions in monosaccharides and the lack of sufficiently convenient and general methods of synthesizing the most important representatives of carbohydrates, namely, amino and deoxy sugars, makes it essential to study the replacement of one of the hydroxyl groups of a monosaccharide by a halogen, which would then open up a route to both deoxy and amino sugars. Up to the present time reactions of this type have only been known for the primary hydroxyl group (at C_6 in hexoses and at C_5 in pentoses); until now, no conditions have been found for replacement of secondary hydroxyl groups in a pyranose or furanose ring by a halogen. In this connection we turned our attention to Rydon's report [1] of the reaction of halogen complexes of triphenyl phosphite of the type $(C_6H_5O)_3PX_2$ (where X = Cl, Br, or I) with the simplest alcohols, which leads to alkyl halides. It might be hoped that this reaction, which proceeds very vigorously and under mild conditions, could be used to replace a hydroxyl group by a halogen in a monosaccharide molecule. As the first substance for testing this possibility in carbohydrates we chose 1,2 : 5,6-diisopropylideneglucofuranose (I), which has only one free hydroxyl group that is attached to C_3.

The reaction of I with the bromine complex of triphenyl phosphite in absolute benzene proceeded readily and spontaneously at room temperature with hardly any evolution of hydrogen bromide. The reaction product, which was obtained after appropriate treatment and removal of the isopropylidene blocking groups by hydrolysis with dilute acid, was a mixture of sugars, the major component of which corresponded in R_f value to the bromodeoxyhexose (II). The latter substance could actually be isolated in 16% yield by partition chromatography of the total sugars formed on cellulose. Completely analogously, the reaction of I with the iodine complex of triphenyl phosphite yielded the iododeoxyhexose (III).

To determine the structure of the halohexoses obtained, we studied their conversion to the corresponding deoxy sugars by hydrogenolysis of the halogen atom in the presence of Raney nickel. Hydrogenation of the bromo (II) and iodo (III) derivatives yielded the same deoxy sugar (IV) and after oxidation of this with periodic acid on a paper chromatogram, it was possible to identify only acetaldehyde, but no malondialdehyde. In exactly the same way, the destruction of the deoxy sugar IV by Ruff's method yielded a single product, differing from 2-deoxyribose, and after oxidation of this on a paper chromatogram with periodic acid, we also identified only acetaldehyde and no malondialdehyde. These results indicate that the deoxy sugar IV was not 3-deoxyglucose, but 6-deoxyglucose (D-chinovose) and, consequently, the product of the initial reaction was not the expected 3-haloglucose, but the 6-haloglucose. In order to eliminate conclusively doubts in connection with the possible change in structure of the halo sugar during the hydrolysis and subsequent treatment, we hydrogenolyzed the reaction product obtained immediately after reaction of I with the bromine complex of triphenyl phosphite, without isolation of the latter from the reaction mixture. After removal of the hydrogen halide and solvent, the reaction mass was hydrogenated in methanol over Raney nickel in the presence of a slight excess of caustic alkali. When

all the alkali was added to the reaction mixture before the beginning of hydrogenation, the hydrogenation was complicated and by means of paper chromatography it was shown that in addition to D-chinovose and starting glucose, the reaction products after hydrolysis also contained a considerable amount of a substance with a higher R_f value, which arose either as a reaction byproduct or as a product from the further conversion of II or IV. On the other hand, if the alkali was added gradually during the hydrogenation, the process proceeded very smoothly and formed almost exclusively IV with a small amount of glucose and the byproduct indicated above. In this case, the D-chinovose was isolated after hydrolysis by means of chromatography on cellulose and identified as the osazone, which had properties corresponding to literature data. On the other hand, the tetraacetate of the iodo derivative (III) was prepared and this corresponded in properties to the α-tetraacetate of 6-iodo-6-deoxyglucose. This demonstrates conclusively that in the reaction of diacetoneglucose with halogen derivatives of triphenyl phosphite, the hydroxyl group of glucose in position 6 is replaced by halogen. Thus, the conversions described above may be represented by the following scheme:

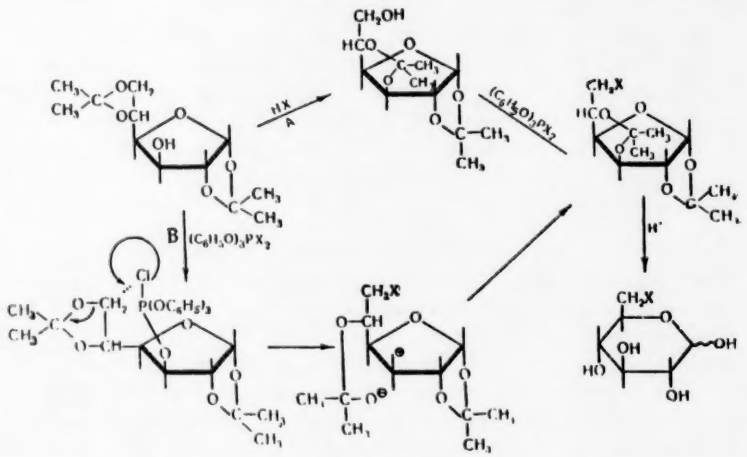


It should be noted that the same result was obtained by Smith [2] by treating I with phosphorus pentachloride, when it was found that 6-chloro-6-deoxyglucose was formed; it was recently stated that an analogous substitution at C_6 occurs during the action of acetobromoglucose on I in the presence of mercury cyanide [3]. At present we have insufficient data to make a definite choice between the two possible reaction routes:

1) As a result of acid-catalyzed migration of an isopropylidene group (the reverse is possible), I forms 1,2 : 3,5-diisopropylideneglucofuranose, which then reacts with replacement of the freed hydroxyl at C_6 (route A);

2) Direct substitution at C_6 with simultaneous displacement of the isopropylidene group by a reaction with transfer of the reaction center according to the scheme proposed previously by Smith (route B). However, it should be remembered that this scheme was not based on any experimental data.

The data presented show that the use of halogen complexes of triphenyl phosphite for replacement of a hydroxyl group in monosaccharides is quite interesting even if it is not of great preparative interest.



EXPERIMENTAL

The R_f values given are average values obtained on ascending chromatograms in the solvent system n-butanol–water–acetic acid (4 : 2 : 1), which was also used for partition chromatography on cellulose. Chromatography paper "M" of Leningrad factory No. 2 was used. The spots were detected with p-anisidine–H_3PO_4 and the

structure of the deoxy sugars demonstrated with a 2.5% solution of $NaIO_4$ in combination with nitroprusside or p-nitroaniline reagents [4].

6-Bromo-6-deoxyglucose. To 9.3 g (0.03 mole) of triphenyl phosphite was added a solution of 2.4 g (0.015 mole) of bromine in 25 ml of absolute benzene and when heat evolution stopped, to the precipitated complex was added a benzene solution of 7.8 g (0.03 mole) of diacetoneglucose; the mixture was shaken for a short time until a homogeneous solution was formed and then left for 48 hr at room temperature. The reaction mixture was then poured into an equal volume of 2 N NaOH, the benzene layer washed with water and evaporated in vacuum, a solution of 2 ml of conc. H_2SO_4 in 200 ml of 50% methanol added, and the mixture boiled for 4 hr. At the end of the heating, the aqueous methanol layer was accurately neutralized with $Ba(OH)_2$ solution, centrifuged, boiled briefly with activated charcoal, and the colorless, neutral solution evaporated in vacuum. The solid mass obtained in this way (3.9 g) was a mixture of sugars whose main component had R_f 0.48. Chromatography on cellulose gave chromatographically pure 6-bromo-6-deoxyglucose in a yield of 1.2 g (16.5%).

6-Iodo-6-deoxyglucose. This was obtained analogously to the 6-bromo derivative from 6.5 g (0.025 mole) of diacetoneglucose with alcohol-free, dry chloroform used as solvent. After chromatography on cellulose, the yield of chromatographically pure product was 1.53 g (21%) and it had R_f 0.56.

α-Tetraacetyl-6-iodo-6-deoxyglucopyranose. A solution of 0.5 g of 6-iodo-6-deoxyglucose in a mixture of 14 g of acetic anhydride and 7 g of glacial acetic acid was cooled to 0°, 16 drops of conc. H_2SO_4 added, and the solution left at 0° for 24 hr. The solution obtained was poured into ice water, the α-tetraacetate formed extracted with chloroform, the chloroform evaporated in vacuum, and the residue recrystallized three times from methanol and dried in high vacuum. The yield was 0.08 g and the m.p. 177.5-178°. Literature data: m.p. 182° [5].

6-Deoxyglucose (D-chinovose). a) An aqueous solution of 1 g of 6-iodo-6-deoxyglucose and 0.5 g of $NaHCO_3$ was hydrogenated for two days over Raney nickel at room temperature with the carbon dioxide formed absorbed by solid KOH. The catalyst was removed by filtration and without isolation, the D-chinovose formed was degraded by Ruff's method by the addition to the solution of 3 g of iodine, followed by the dropwise introduction of a solution of 1.4 g of NaOH in 50 ml of water with stirring. The solution was left for 20 min, then acidified with dilute H_2SO_4, the liberated iodine extracted with carbon tetrachloride, and the aqueous solution neutralized with silver carbonate, treated with a large excess of KU-1 cationite in the H^+ form, neutralized with $Ca(OH)_2$, and evaporated to 10 ml in vacuum. To the solution was added 0.11 g of $Ba(OCOCH_3)_2$ and 0.06 g of $Fe_2(SO_4)_3$, the mixture heated to boiling, the precipitate removed by filtration, and the filtrate cooled to 40° and treated with 0.7 ml of 30% H_2O_2. When heat evolution and the vigorous liberation of gases ceased and the temperature again fell to 40°, a further 0.7 ml of 30% H_2O_2 was added, air sucked through the solution under reduced pressure for 15 min to remove volatile products, and the mixture diluted with an equal volume of methanol and centrifuged. The only product in the centrifuged solution was a sugar with R_f 0.50, and when this was oxidized on paper with $NaIO_4$, we detected only acetaldehyde and no malondialdehyde [4]; 2-deoxy-D-ribose taken for comparison had R_f 0.39.

b) To 3.1 g (0.01 mole) of triphenyl phosphite was added a solution of 0.8 g (0.005 mole) of bromine in 10 ml of benzene and then, with cooling to 0°, a benzene solution of 2.6 g (0.01 mole) of diacetoneglucose (see Expt. 1). At the end of the reaction, the benzene solution was washed with NaOH solution and water and evaporated The residue was dissolved in 30 ml of absolute methanol and hydrogenated at room temperature over Raney nickel with a solution of 0.6 g of KOH added dropwise during the hydrogenation until the absorption of hydrogen ceased. The catalyst was removed by filtration, the filtrate neutralized with dilute H_2SO_4 and evaporated in vacuum, and the residue dissolved in a mixture of 50 ml of 50% methanol and 0.5 ml of conc. H_2SO_4 and boiled for 4 hr. The cooled solution was neutralized with $Ba(OH)_2$, the precipitate removed by filtration, the solution boiled with a small amount of activated charcoal, the charcoal removed, and the filtrate evaporated. Chromatography of the residual sirup on cellulose yielded 0.2 g (8% of theoretical) of D-chinovose with R_f 0.36.

If all the alkali was added at the beginning in the hydrogenation, considerable amounts of a substance of unknown structure with R_f 0.70 were formed as a byproduct. This process was suppressed with the gradual addition of alkali.

D-Chinovose phenylosazone. To a mixture of 2.5 ml of 4 N acetic acid and 0.5 g of phenylhydrazine was added a solution of 0.2 g of D-chinovose in 2 ml of water, the mixture boiled for 30 min in a stream of CO_2, and

the light yellow precipitate collected from the cooled mixture and dried to give 0.2 g of material with m.p. 175-176° (from aqueous alcohol with rapid heating). $[\alpha]^{20}D$ −75.5 ± 2° (c 2, alcohol–pyridine, 3 : 2).

	Found %	C 63.29; 63.25; H 6.54; 6.52
$C_{18}H_{22}O_3N_4$.	Calculated %	C 63.14; H 6.48

Literature data [6]: m.p. 189-191°; $[\alpha]^{20}D$ −77° (c 2, alcohol–pyridine, 3 : 2).

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CATALYTIC DEHYDROGENATION OF ISOPENTANE

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The dehydrogenation of isopentane over chromium–aluminum oxide catalysts over the temperature range 500-600° was investigated. The main feature of the work was the use of a fluidized bed for investigating the kinetics of the process.

The plan of the vacuum apparatus with the fluidized bed of catalyst is illustrated in Fig. 1. The reactor (1) was a quartz tube, 21 mm in diameter, with a wide section at the top and an electrical heating spiral. The catalyst (10-20 ml), which had a grain size of 0.05-0.1 mm, was placed on a quartz packing, lying on a chamotte

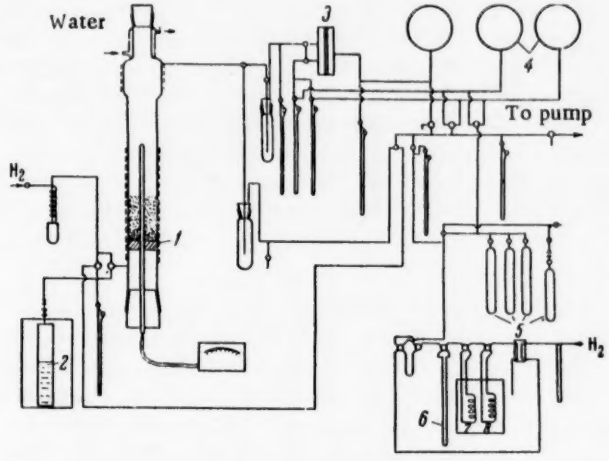

Fig. 1. Plan of vacuum apparatus with fluidized bed of catalyst.

porous plug attached to a thermocouple pocket. The catalyst was first dried in a stream of air and was then activated with hydrogen for an hour. The isopentane, which was chromatographically pure, was admitted to the reactor from a thermostatted tank (2). The fluidized bed was created when the isopentane was passed through the catalyst. Extrainment of gas by the particles led to equalization of the temperature and gas mixture composition throughout the length of the bed. Special experiments showed that under the conditions in the reactor there was almost complete mixing of the gas [1, 2], when the composition of the gas was the same throughout the bed. The reaction products passed through a tap (3) for maintaining the pressure [3] (which was found very effective

Dehydrogenation of Isopentane in Stationary and Fluidized Beds

	Stationary bed (p = 760 mm)							Fluidized bed (p = 100 mm)			
	catalyst No. 1			catalyst No. 2			catalyst No. 3	catalyst No. 2			
	520°	550°	580°	520°	550°	580°	550°	580°		600°	
	space velocity, vol/vol·hr										
	1,04	1,12	2,74	1,15	0,96	2,30	0,95	0,50	1,01	0,35	0,79
Conversion of isopentane, %	28,1	47,0	60,7	27,6	45,5	54,3	46,5	50,3	39,1	62,2	50,4
Selectivity, %	79,3	65,6	61,7	81,9	66,3	69,0	65,9	63,2	65,9	57,0	59,4
Consumption of isopentane in the formation of reaction products, mol.% isoamylenes	21,2	28,5	33,0	21,2	27,6	32,8	29,2	21,0	16,0	20,2	17,7
3-methylbutene-1	3,1	2,9	4,2	2,9	2,5	5,0	2,4	1,9	1,7	1,5	1,4
2-methylbutene-1	5,7	8,5	10,4	6,6	9,3	9,8	8,9	7,7	5,2	6,8	5,9
2-methylbutene-2	12,4	17,1	18,4	10,7	15,8	18,0	17,9	12,4	9,1	11,9	10,4
isoprene	1,1	2,3	4,5	1,3	2,5	4,6	1,4	10,8	9,8	15,3	12,2
$n\text{-}C_5 + C_6$	2,6	5,2	8,3	1,5	5,3	5,2	3,0	3,9	1,9	3,4	2,9
Coke	0,7	1,6	2,8	0,4	1,1	2,5	2,7	6,8	3,5	7,0	6,2
$C_1\text{-}C_4$ hydrocarbons	2,5	9,4	12,1	3,2	9,0	9,2	10,2	7,8	7,9	16,3	10,4

under analogous conditions [4]) into previously evacuated flasks (4) and then they were introduced into a chromatography apparatus. The total content of C_2 and higher hydrocarbons was found by measuring the pressure in the receivers (5) before and after separation of the gases which were not condensed by liquid nitrogen. Air and methane were separated on columns with activated charcoal (6) with hydrogen used for displacement and the hydrogen content was found from the difference between the amount of uncondensed gases and the amount of air and methane. The $C_2\text{-}C_5$ hydrocarbons were separated on columns with diisoamyl phthalate (7) and acetonylacetone (8) by the procedure described in [5]. The analysis procedure made it possible to find the individual composition of the mixture of C_5 hydrocarbons with a relative accuracy of 3-4%. When the products were fractionated on a column with an efficiency of 30 theoretical plates, no hydrocarbons boiling above 40° were detected, but the chromatogram showed the peak of an unidentified C_6 hydrocarbon. In the balance, we considered only hydrocarbons which appeared on the chromatogram. In addition to experiments with a fluidized bed, we also carried out a series of experiments with a stationary bed of catalyst with a grain size of 0.25-0.50 mm under conditions which are normally used for studying such reactions [6-9] (see Table 1). Catalyst No. 1 contained 10.2 mol. percent Cr_2O_3, 88.1 mol. percent Al_2O_3, and 1.7 mol. percent K_2O. Catalyst No. 2 contained 7.0 weight percent Cr_2O_3, 92.5 weight percent Al_2O_3, and 0.5 weight percent K_2O. The properties of catalyst No. 3 were described in [6].

As follows from the table, the catalysts of varied composition investigated had similar activity. At 550° with a space velocity of the order of 1, the yield of isoamylenes on the isopentane passed was 27.6-29%, the yield of isoprene 1.5-2.5%, the degree of conversion of isopentane 46-47%, and the selectivity, calculated as the ratio of the yield of isoamylenes and isoprene to the reacted isopentane, was 65-67%. With an increase in temperature to 580°, the yield of isoamylenes increased to 31-33%, the isoprene yield rose to 3.5-4.6%, and the maximum selectivity was 65-70%. At 520° and a space velocity of $\sim 1\ hr^{-1}$, the isopentane conversion equaled 28% and the yield of isoamylenes and isoprene was 23%.

Experiments with a fluidized bed at reduced pressures and comparative kinetic experiments with a stationary bed at atmospheric pressure were carried out on catalyst No. 2. The experimental conditions were as follows: temperature, 500 and 550°; pressure, 100-500 mm Hg in the fluidized bed and 760 mm in the stationary bed. The isoprentane conversion did not exceed 30%.

Figures 2 and 3 show typical product distribution curves. The degree of isopentane conversion is plotted along the abscissa axis (y), and the difference in ordinate between two neighboring curves, Δy, equals the relative number of moles of isopentane consumed in the formation of a product. At $y < 0.3$, the composition of the

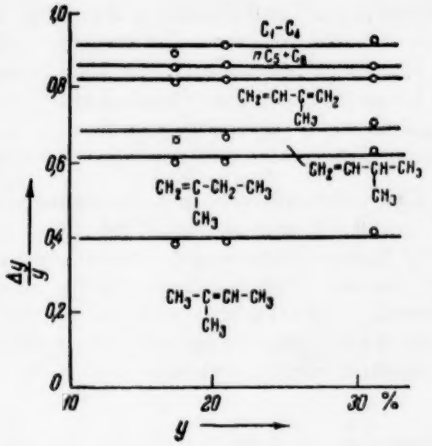

Fig. 2. Distribution of reacted isopentane among reaction products at 550° and 300 mm Hg in a fluidized bed.

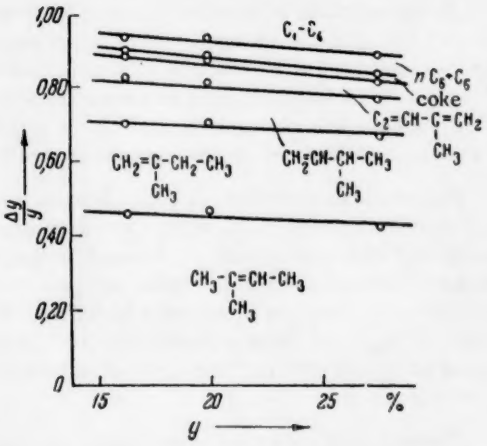

Fig. 3. Distribution of reacted isopentane among reaction products at 520° and atmospheric pressure in a stationary bed.

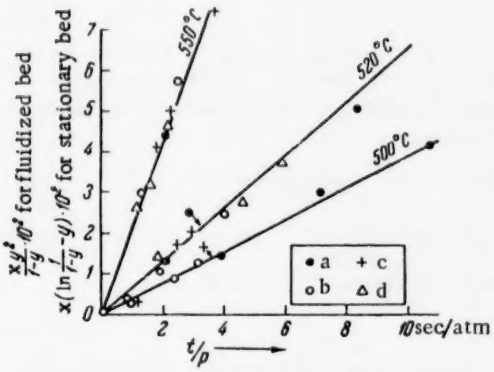

Fig. 4. Kinetic curves of isopentane dehydrogenation at low conversions: a) 100 mm Hg, fluidized bed; b) 300 mm Hg, fluidized bed; c) 500 mm Hg, fluidized bed; d) atmospheric pressure, stationary bed.

products changed little with the degree of conversion. The molar ratios of $C_1 : C_4$ and $C_2 : C_3$ in gases were close to unity and evidently these hydrocarbons were formed by cracking of isopentane. The portion of the total amount of reacted isopentane consumed in cracking was 2-4% at 500°, 3-10% at 520°, and 6-12% at 550°, and the fall in selectivity with a rise in temperature corresponded approximately to the increase in consumption of isopentane in cracking.

2-Methylbutene-2, 2-methylbutene-1, and 3-methylbutene-1 were present in the products in the ratio of 100 : 50 : 16 at 500°, 100 : 54 : 18 at 520°, 100 : 55 : 16 at 550°, and 100 : 56 : 14 at 580°. This ratio depended little on the pressure and conversion of isopentane and differed insignificantly from the equilibrium ratio. Within the limits of experimental error, the ratio of isoprene to the sum of the isoamylenes coincided with the equilibrium value. Hence it follows that the isomerization and dehydrogenation of isoamylenes on oxide catalysts proceed at a high rate.

In processing the experimental data in the region of degrees of conversion up to 30%, we used the equations

$$\frac{xy^2}{1-y} = K\frac{t}{p} \quad \text{for a fluidized bed;} \tag{1}$$

$$x\left(\ln\frac{1}{1-y} - y\right) = K\frac{t_0}{p} \quad \text{for a stationary bed,} \tag{2}$$

where y is the degree of isopentane conversion, x is the selectivity (number of moles of isopentane consumed in the formation of isoamylenes and isoprene at y = 1), p is the pressure, t is the contact time (ratio of catalyst volume to the volume of starting isopentane under the experimental conditions), and K is a constant.

From Fig. 4 it follows that the experimental points lie about lines 1 and 2, whose slope relative to the t/p axis equals the constant K, independent of pressure; the mean deviation of the experimental points from the lines is 5%.

In the derivation of equations (1) and (2), we used the ideas in [10, 11] on the course of irreversible reactions on a homogeneous surface; in the region of degrees of conversion up to 30%, the rate of the reverse reaction did not exceed 4-6% of the rate of the forward reaction. These equations correspond to the case where isoamylenes and isoprene are strongly adsorbed on the surface with identical adsorption coefficients. Equation (1) characterizes the state of complete mixing of the gas. In the derivation of equation (2), it was assumed that there was no mixing and also no allowance was made for the change in stoichiometry of the process with the degree of conversion.

Systematic deviations of the points from the lines in Fig. 4 due to the difference in the adsorption coefficients of the reaction products, which exceed the experimental error, should have occurred if the ratio of the adsorption coefficients of isoprene and isoamylenes had exceeded 2. Thus, it follows from the experiment that this ratio did not exceed 2 on the chromium catalyst. In exactly the same way it can be deduced that the adsorption coefficient of isoamylenes is two orders higher than that of isopentane. The value of K found from the slope of the lines in Fig. 4 was found to equal $3.87 \cdot 10^{-3}$, $6.72 \cdot 10^{-3}$, and $21 \cdot 10^{-3}$ sec/atm for temperatures of 500, 520, and 550°, respectively. The observed activation energy, calculated from the Arrhenius equation, was 44,000 cal/mole.

Comparison of the experimental results for fluidized and stationary beds shows that:a) in the first case there is complete mixing of the gas; b) in the second case the process occurs in the kinetic region (particle size up to 0.5 mm, temperature 550°) since it is described by identical equations on coarse and fine particles.

The table gives the results of experiments on the dehydrogenation of isopentane at elevated temperatures and reduced pressures. At 600°, 100 mm Hg, and a space velocity of 0.35, of 62.2% of decomposed isopentane, 20.2% was converted into isoamylenes and 15.3% into isoprene, while the isoprene content of the C_5 fraction was 21%.

Complete mixing of the gas in the reactor should have led to a decrease in the isoprene yield due to an increase in the proportion of secondary and side reactions. In the technical realization of the process under conditions where mixing may be decreased either by a change in the hydrodynamic state of the bed or by sectionalizing of the reactor, it is possible to obtain a higher yield of isoprene.

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SEMIEMPIRICAL METHOD OF CALCULATING HEATS OF FORMATION OF HYDROPEROXIDES AND CONJUGATION ENERGIES OF SOME PEROXIDE RADICALS

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In the oxidation of a wide range of organic substances in the gas, liquid and solid phases, hydroperoxides play an essential role as branching agents. To calculate the energetics of reactions involving hydroperoxides it is necessary to have information on the heats of formation of these compounds. However, the experimental data available at the present time are few and do not cover the most interesting compounds.

There are various semiempirical methods of calculating the heats of formation of molecules [1, 2]. The inadequacy of experimental data on ΔH of hydroperoxides and, in particular, the almost complete lack of such data for the first members of homologous series makes it impossible to use these methods with any reliability for calculating the heats of formation of organic hydroperoxides.

The method we propose is based on the following considerations. According to the ideas developed by N. N. Semenov [3, 4], the energy of a bond X-Y (Q_{XY}) may be represented in the following way $Q_{XY} = E_{XY} - B_X - B_Y$, where E_{XY} is the energy of rupture of the bond of X and Y with the assumption that the electronic configuration of the free X and Y remains the same as in the starting molecule and B_X and B_Y are the conjugation energies of the radicals X and Y. Thus, for compounds of the type XOOX and $XOO^{\cdot}$, we may write the equations:

$$Q_{X-OOX} = E_{OX} - B_X - A_1; \quad (1)$$

$$Q_{X-O_2^{\cdot}} = E_{OX} - B_X - A_2; \quad (2)$$

$$Q_{XO-C^{\cdot}} = E_{OO} - B_{OX} + A_1, \quad (3)$$

where A_1 is the conjugation energy of the radical $XO_2^{\cdot}$, while A_2 is the transition energy of the O_2 molecule obtained by elimination of X from $XO_2^{\cdot}$ in an actual stable state. From the Law of Conservation of Energy it follows that regardless of the nature of X the following identity should be observed:

$$A_1 + A_2 = A_1^0 + A_2^0 = \text{const}, \quad (4)$$

where $A_1^0 + A_2^0$ is the sum of the energies of the two three-electron bonds in the oxygen molecule.

In actual fact, the transition from the XOOX state to the $2X + O_2$ state may be achieved by two methods: a) by simultaneous rupture of both OX bonds with the expenditure of energy:

$$q = 2E_{OX} - (A_1^0 + A_2^0) - 2B_X; \quad (5)$$

Bond Energies in Compounds of the Type XOOX and $XO_2^{\cdot}$ (kcal)

Compound	Q_{X-OOX}	$Q_{X-O_2^{\cdot}}$	$Q_{XO-O^{\cdot}}$	Method of selecting E
HOOH	89,5	47	62	$E_{OH} = {}^1/_2(Q_{H-OH} + Q_{OH})$
ClOO	—	4,3	63,7	$E_{OO} = Q_{HO-OH} - 2B_{OH}$
$ClOO_2$	—	−6	48,8	$E_{OCl} = {}^1/_2(Q_{Cl-OCl} + Q_{O-Cl})$
RO_2	—	14	—	1) $E_{CO} = Q_{R-OH} + B_R + B_{OH}$ 2) From the activity of OH in reactions at the bonds C-C and C-H

and b) by successive elimination of X from XOOX and $XO_2^{\cdot}$ with the expenditure of energy

$$q = Q_{X-O_2X} + Q_{X-O_2^{\cdot}}. \tag{6}$$

A combination of equations (1), (2), (5), and (6) gives equation (4), which may be regarded as a thermodynamic criterion of the fact that all the compounds examined correspond to the chemical formulas assigned to them, are in thermochemical conformity, and obey the law of additivity.

The numerical calculation of A_1 and A_2 from equations (1), (2), and (3) was carried out for cases where X = H, Cl, ClO, R, and F,* where R is a hydrocarbon radical. The data used in the calculations [3, 8] are given in the table.

Figure 1 shows that the value

$$A_1 + A_2 = A_1^0 + A_2^0 = 82 \pm 2 \text{ kcal} \tag{4'}$$

and is independent of the nature of X.

Equation (4') makes it possible to calculate the heats of formation of hydroperoxides. By expressing the heat effects of the reactions

$$RH + O_2 \rightarrow ROOH + Q_1;$$
$$RH + {}^1/_2O_2 \rightarrow ROH + Q_2$$

through the energies of the corresponding bonds, it is possible to write:

$$Q_1 = \{E_{CO} + E_{OH} - E_{CH}\} + \{B_{R(H)} - B_{R(O)}\} - (A_1 + A_2); \tag{7}$$
$$Q_2 = \{E_{CO} + E_{OH} - E_{CH}\} + \{B_{R(H)} - B'_{R(O)}\} - {}^1/_2(A_1 + A_2 + E_{OO}), \tag{8}$$

where $B_{R(H)}$, $B_{R(O)}$, and $B'_{R(O)}$ are the conjugation energies of the radical R obtained from RH, ROOH, and ROH.

By combining (7) and (8) and assuming that $B_{R(O)}$ and $B'_{R(O)}$ are equal, we obtain the expression:

$$\Delta H_{ROOH} = \Delta H_{ROH} + {}^1/_2(A_1 + A_2 - E_{OO}) = \Delta H_{ROH} + 23 \text{ kcal} \tag{9}$$

As Fig. 2 shows, points corresponding to experimental data [5, 6] lie well on the line calculated from this equation.

The constancy of the values $A_1 + A_2$ for different compounds and the applicability of relation (9) to hydroperoxides of different classes makes it possible to calculate quite reliably the heats of formation of hydroperoxides

*The value of $A_1 + A_2$ for the compound ClO_2F was calculated from kinetic data.

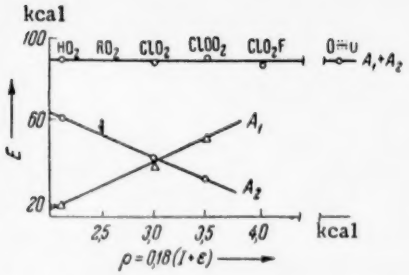

Fig. 1. Relation of A_1, A_2, and $A_1 + A_2$ to the electronegativity of the atom directly attached to oxygen.

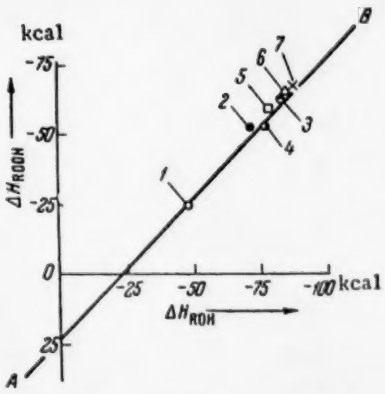

Fig. 2. Relation of ΔH_{ROOH} to ΔH_{ROH}. AB) Theoretical line; experimental points for R: 1) Tetralyl-1; 2) cyclohexyl, 3) methylcyclohexyl; 4) tert-butyl; 5) n-hexyl; 6) decalyl; 7) n-heptyl.

for which there are no experimental data from comparison with the known heats of formation of the corresponding alcohols, which, in its turn, makes it possible to calculate the energy of rupture of O-O bonds in hydroperoxides, as the heats of formation of a series of alkoxyl radicals are known at the present time [5].

The calculation shows that with an increase in the length and branching of the hydrocarbon chain, Q_{RO-OH} increases regularly from 32 kcal for CH_3OOH to 39 kcal for tert-$C_5H_{11}OOH$.

From Fig. 1 it follows that the conjugation of peroxide radicals falls with a decrease in the electronegativity of the atom directly attached to the oxygen, according to the equation

$$A_1 = -27 + 22{,}5\rho.$$

Apparently, with a decrease in the electronegativity of X, there is an increase in the lability of the adjacent σ-bond and consequently its capacity to enter into conjugation with the unpaired electron, which leads to destabilization of the three-electron bond in the peroxide radical.

It is interesting to note that expression (4') makes it possible to calculate the conjugation energy of peroxide radicals for cases where A_2 may be determined from the heat of the reaction $R + O_2 \rightarrow RO_2 + q$. This calculation was carried out for the peroxide radical formed after irradiation of Teflon with γ-rays in the presence of oxygen according to [7]. The conjugation energy of this radical was found to equal 25 ± 2.5 kcal.

Equation (4') also makes it possible to analyze the structure of a series of polyoxygen compounds.

In particular, it is readily shown that neither the biradical form, nor the three-membered ring form corresponds to the true structure of ozone, as criterion (4') is not observed in these cases.

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FERROCENYLMETHYLLITHIUM

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We previously [1] described the preparation of ethers of ferrocenylcarbinol from N,N-dimethylaminomethylferrocene iodomethylate. In the present work we were able to cleave the methyl ether of ferrocenylcarbinol with lithium and used the ferrocenylmethyllithium thus obtained for preparing ferrocene derivatives. In addition, we found that ethers of ferrocenylcarbinol are readily obtained by heating ferrocenylcarbinol with appropriate alcohols in the presence of acetic acid.

$$C_5H_5FeC_5H_4CH_2OH + ROH \xrightarrow{CH_3COOH} C_5H_5FeC_5H_4CH_2OR + H_2O.$$

By this method we prepared the methyl, ethyl, and benzyl ethers of ferrocenylcarbinol in yields of 73, 80, and 72%, respectively.

The ease of formation of ethers of ferrocenylcarbinol is explained by the stability of the ferrocenylmethyl carbonium ion [2].

We cleaved the methyl ether of ferrocenylcarbinol with lithium in tetrahydrofuran. This gave a high yield of ferrocenylmethyllithium, which could not be obtained by other methods.

$$C_5H_5FeC_5H_4CH_2OCH_3 + 2\,Li \rightarrow C_5H_5FeC_5H_4CH_2Li + CH_3OLi.$$

The reaction conditions were analogous to those described by Gilman et al. [3] for the cleavage of benzyl ethers. The ferrocenylmethyllithium yield was more than 80%, judging by the amount of methylferrocene formed by hydrolysis.

Ferrocenylmethyllithium reacts smoothly with trimethylchlorosilane to give (ferrocenylmethyl)-trimethylsilate in 68% yield.

$$C_5H_5FeC_5H_4CH_2Li + ClSi(CH_3)_3 \rightarrow C_5H_5FeC_5H_4CH_2Si(CH_3)_3 + LiCl.$$

The action of anhydrous ferric chloride on ferrocenylmethyllithium results in combination of the radicals in pairs to form 1,2-diferrocenylethane, which was identical with that formed by condensation of ferrocene with formaldehyde in the presence of sulfuric acid [4, 5].

$$C_5H_5FeC_5H_4CH_2Li \xrightarrow{FeCl_3} C_5H_5FeC_5H_4CH_2CH_2C_5H_4FeC_5H_5.$$

EXPERIMENTAL

Methyl ether of ferrocenylcarbinol. To a solution of 3.24 g (0.015 mole) of ferrocenylcarbinol [6] in 90 ml of absolute methanol was added 2.7 ml of glacial acetic acid. The solution was heated for 5 hr on a water bath, then cooled and 100 ml of ether added. The ether–alcohol solution was washed with water (2 × 300 ml),

10% sodium carbonate solution, and again with water and dried with $MgSO_4$. The solvent was removed and the methyl ether of ferrocenylcarbinol vacuum distilled twice. The yield was 2.52 g (73% of theoretical). The product had b.p. 106-107.5°/1.5 mm; $n^{20}D$ 1.6003. The constants coincided with those we described previously [1].

The ethyl ether of ferrocenylcarbinol was prepared analogously to the methyl ether. The heating time was increased to 6 hr. The yield was 80% of theoretical. The constants coincided with those we described previously [1]. The compound had b.p. 112-113.5°/2 mm; $n^{20}D$ 1.5855.

The benzyl ether of ferrocenylcarbinol was prepared analogously to the ethyl ether and was purified by chromatography on Al_2O_3. The yield was 73% of theoretical. Its melting point and a mixed melting point with previously prepared ether [1] were 88-89°.

Ferrocenylmethyllithium.• To a mixture of 0.7 g (0.1 g-at) of lithium turnings•• and 8 ml of absolute tetrahydrofuran, freshly distilled over Na,••• was added a solution of 1.15 g (0.005 mole) of the methyl ether of ferrocenylcarbinol in 7 ml of tetrahydrofuran over a period of 45 min with stirring and cooling to -7 to -5°. After approximately half of the ether solution had been added, the reaction mixture became slightly turbid and red spots appeared on the lustrous surface of the lithium, indicating the beginning of the reaction. If the reaction did not begin when half of the ether had been added, the temperature was raised to 0° for a few minutes. When all the ether had been added, stirring was continued for 1 hr at -5°. The dark red solution of ferrocenyllithium formed was then filtered under nitrogen to remove excess lithium for certain experiments.

Hydrolysis of ferrocenylmethyllithium. A solution of ferrocenylmethyllithium, obtained by the method described above from 2.3 g (0.01 mole) of the methyl ether of ferrocenylcarbinol and 1.4 g of lithium, was poured into a mixture of 10 g of ice and 3 g of NH_4Cl. The methylferrocene was extracted with ether. The ether solution was washed with water and dried with $CaCl_2$. Removal of the solvent and recrystallization from methanol yielded 1.64 g of methylferrocene. The yield was 82% of theoretical, calculated on the starting methyl ether of ferrocenylcarbinol. The m.p. of the methylferrocene and a mixed melting point with a sample obtained previously [7] were 35-36°.

(Ferrocenylmethyl)-trimethylsilane. Over a period of 15 min, a solution of 4 ml (3.4 g, 0.02 mole) of trimethylchlorosilane in 8 ml of tetrahydrofuran was added with stirring to a solution of $C_5H_5FeC_5H_4CH_2Li$, obtained from 4.6 g (0.02 mole) of the methyl ether of ferrocenylcarbinol and 2.8 g of Li; the temperature of the reaction mixture was -5 to -3°. Stirring was continued for 10 min with cooling to 0°, for 1 hr at room temperature, and for 1 hr at the boiling point. The reaction mixture was then cooled and poured into water (150 ml) after removal of the excess lithium. The (ferrocenylmethyl)-trimethylsilane was extracted with benzene. The benzene solution was washed several times with water and dried with anhydrous magnesium sulfate. Removal of the benzene gave 4.4 g of a red-brown oily product, which was chromatographed on Al_2O_3. The (ferrocenylmethyl)-trimethylsilane was eluted with ligroin and recrystallized twice from absolute CH_3OH. The yield was 3.6 g (68.5% of theoretical.) The m.p. was 46.5-47.5°.

	Found %:	C 61.79; 61.72; H 7.35; 7.41
$C_{14}H_{20}FeSi$.	Calculated %:	C 61.76 H 7.41

Action of $FeCl_3$ on ferrocenylmethyllithium. Over a period of 20 min, a solution of 1.62 g (0.01 mole) of anhydrous $FeCl_3$ in 50 ml of absolute ether was added with stirring and cooling to -30° to a solution of ferrocenylmethyllithium, prepared from 1.4 g (0.02 mole) of $C_5H_5FeC_5H_4 \cdot CH_2OCH_3$ and 1.4 g of lithium. Stirring was then continued for 1.5 hr at room temperature and the mixture poured through a fine copper sieve(to remove lumps of lithium)onto ice and NH_4Cl. The ether layer was separated. To the aqueous layer was added conc. HCl and 2.5 g of $SnCl_2$, after which the mixture was extracted with benzene until the extracts were colorless. The ether and benzene solutions were combined, washed with water, 10% sodium carbonate solution, and again with water, and dried with $CaCl_2$. The solvent was removed in vacuum and to the residue was added 15 ml of ligroin. The precipitated 1,2-diferrocenylethane was collected by filtration, washed with ligroin, and recrystallized from ether. The weight was 0.6 g. The m.p. was 196-197.5°. In a sealed tube under vacuum it had m.p. 200-200.5°.

•The preparation of ferrocenylmethyllithium and all reactions with it were carried out in an atmosphere of pure nitrogen.

••The quality of the lithium apparently plays an important part. Thus, no reaction occurred with one sample of lithium.

•••The tetrahydrofuran was first distilled over KOH and three times over metallic sodium.

Found %: C 66.29; 66.40; H 5.62; 5.82; Fe 27.98; 27.88

$C_{22}H_{22}Fe$. Calculated %: C 66.36; H 5.63; Fe 28.05

Literature data for 1,2-diferrocenylethane [4]: m.p. 193-195°.

After separation of the diferrocenylethane, the ligroin solution was chromatographed on Al_2O_3. Ligroin was used to elute 0.7 g of methylferrocene; a mixture of benzene and ligroin (2 : 1) eluted 0.08 g of diferrocenylethane, and benzene and ether gave a small amount of ferrocenylcarbinol with m.p. 79-80°, a mixture of which with a sample obtained from N,N-dimethylaminomethylferrocene iodomethylate [6] melted without depression. The total yield of 1,2-diferrocenylethane was 0.68 g (34% of theoretical).

The 1,2-diferrocenylethane we obtained was identical with that formed by condensation of ferrocene with formaldehyde [4, 5] according to the infrared spectrum, and a mixture of the two samples melted without depression (m.p. 196-197.5°).

New data on diferrocenylethanes obtained by condensation of formaldehyde and benzaldehyde with ferrocene [5] and by Friedel–Crafts reactions [8] have been sent to press at the same time.

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ISOTOPIC EXCHANGE BETWEEN DIARYLIODONIUM FLUOBORATES AND ARYL IODIDES LABELED WITH I^{131}

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A. N. Nesmeyanov and his co-workers [1-4] investigated the thermal decomposition of aryldiazonium and diaryliodonium fluoborates in the presence of various organic compounds and thus established that these fluoborates decompose heterolytically with the formation of aryl cations.

$$Ar:N_2^+BF_4^- \rightarrow Ar_2^+ + N_2 + FB_4^-,$$

$$Ar_2I^+BF_4^- \rightarrow Ar^+ + ArI + BF_4^-.$$

The latter attack the position with the highest electron density in organic molecules.

Thus, L. G. Makarova and A. N. Nesmeyanov [4] showed that the thermal decomposition of diphenyliodonium fluoborate in the presence of pyridine, trimethylamine, triphenylphosphine, triphenylarsine, triphenylstibine, diphenyl sulfide, and diphenylselenium forms fluoborates of the corresponding onium compounds.

By decomposing benzenediazonium fluoborate in chlorobenzene and bromobenzene, A. N. Nesmeyanov and his co-workers prepared diphenylchloronium [2] and diphenylbromonium salts [1].

$$C_6H_5N_2BF_4 + C_6H_5X \rightarrow (C_6H_5)_2X^+BF_4^- + N_2.$$

It should be noted that they prepared the diphenyliodonium salt by decomposition of benzenediazonium fluoborate not in pure iodobenzene, but in a mixture of it with acetone [3]. The diphenyliodonium salt was not formed in pure iodobenzene.

As A. N. Nesmeyanov showed, diphenyliodonium [5] and diphenylbromonium salts [3] are also formed in the spontaneous decomposition of double salts of benzenediazonium and mercuric iodides or benzenediazonium and mercuric bromides. In all these cases the phenylhalogenonium compounds are formed by fundamentally the same route: A phenyl cation, arising during the decomposition of benzenediazonium fluoborate in the presence of a halobenzene, adds to the halogen atom through the unshared pair of electrons of the latter. It is evident that a phenyl cation formed during the decomposition of diaryliodonium fluoborate should behave completely analogously. These considerations led us to the conclusion that the isotopic exchange between diaryliodonium fluoborates and aryl iodides described in the present work should be possible.

The isotopic exchange we studied may be represented by the following equation:

$$Ar_2I^+BF_4^- + ArI^* \rightarrow Ar_2I^{*+}BF_4^- + ArI \ (I^* = I^{131}).$$

TABLE 1

Ar_2IBF_4	M.p., °C	Decomp. p., °C	Found, %			Calculated, %			Yield, %
			C	H	F	C	H	F	
$(C_6H_5)_2IBF_4$	136	210	39,11 39,19	2,65 2,68	21,04 21,54	39,17	2,74	20,68	79
$(p\text{-}ClC_6H_4)_2IBF_4$	181,5—182	224	33,14 33,15	1,72 1,73		33,0	1,73		27
$(p\text{-}BrC_6H_4)_2IBF_4$	193,5	217	28,03 28,00	1,55 1,53	14,65 14,60	27,41	1,53	14,45	4
$(p\text{-}CH_3C_6H_4)_2IBF_4$	106,5—108	216	42,07 42,08	3,51 3,68	18,99 19,43	42,46	3,56	19,19	35
$(p\text{-}CH_3OC_6H_4)_2IBF_4$	187	209	39,09 38,95	3,12 2,98	18,13 18,28	39,29	3,30	17,76	69
$(p\text{-}O_2NC_6H_4)_2IBF_4$	199	224	31,43	1,79		31,47	1,76		74
$(p\text{-}C_2H_5OCOC_6H_4)_2IBF_4$	93	224	42,30 42,18	3,67 3,71		42,22	3,54		9

TABLE 2

Ar	Temp., °C	Reaction time, hr	Degree* of exchange, %	Yield, %
C_6H_5	198—202	2	36	66
$p\text{-}ClC_6H_4$	200	2	24	83
		4	49	64
$p\text{-}BrC_6H_4$	200	2	8	85
		4	27	62
		6	30	—
$p\text{-}CH_3C_6H_4$	199	4	16	26
$p\text{-}CH_3OC_6H_4$	181	2	8	89
		4	17	85
	192,5	2	16	76
		4	26	53
$m\text{-}C_6H_5OCOC_6H_4$	181	1	9	45
$m\text{-}O_2NC_6H_4$	183	4	4	83
	192	4	5	60
	200	1	0	79

*Average of a series of experiments carried out under optimal conditions.

The radioactive aryl iodides required for the reaction were prepared by thermal decomposition of diaryliodonium iodide, the anion of which contained iodine labeled with I^{131}.

For the preparation of radioactive diaryliodonium iodide, the iodonium halide was triturated with moist silver oxide, the silver halide removed by filtration, and the aqueous solution of diaryliodonium hydroxide obtained treated with an aqueous solution of radioactive iodine in the form of potassium iodide, sodium iodide, or elementary iodine. A solution of inactive potassium iodide was then added until the diaryliodonium iodide was completely precipitated.

The following procedure was used for determining the activity of the I^{131}-labeled aryl iodide obtained by the method described above. An accurately weighed sample (20 mg) of aryl iodide was deposited on a standard filter, 2 cm in diameter, by solution in 1 drop of acetone and covered with a lacquer of Plexiglas in dichloroethane. When dry, the filter was placed in a tracing paper envelope and the activity measured on a B-2 apparatus with an SI-2B type end-window counter.

The diaryliodonium fluoborates which we used in the reaction were prepared by the method described by L. G. Makarova and A. N. Nesmeyanov [4] for diphenyliodonium fluoborate.

Table 1 gives the Ar_2IBF_4 we synthesized for the first time and their melting points, analyses, and yields. It was found that the isotopic exchange studied occurred only close to the decomposition point of the diaryliodonium fluoborate.

For determination of the degree of exchange, accurately weighed samples of equimolecular amounts of diaryliodonium fluoborate and aryl iodide, labeled with I^{131}, were introduced into a tube with a ground-glass joint. The tube was closed with another tube 25 cm long, which ended in a capillary, and placed in a thermostat with compressor oil. The reaction mixture was kept in the thermostat for a definite time at a constant temperature, which lay within the range of 180-200° (depending on the decomposition point of the diaryliodonium fluoborate).

At the end of the reaction the tube was cooled, the contents washed repeatedly with ether to remove aryl iodide, the residue dissolved in boiling water, and the solution filtered. The filtrate was evaporated to a small volume and cooled. The precipitated diaryliodonium fluoborate was collected by filtration, washed with water and ether, and dried in a vacuum desiccator.

The activity of the diaryliodonium fluoborate was determined analogously to the activity of the aryl iodide. The yield of diaryliodonium fluoborate obtained as a result of the isotopic exchange was determined in parallel with the activity determination. For this purpose the aqueous solution of Ar_2IBF_4 was evaporated to dryness and the residual iodonium salt weighed.

We studied the isotopic exchange of diphenyliodonium fluoborate with iodobenzene, of di-(p-chlorophenyl)-iodonium fluoborate with p-chloroiodobenzene, of di-(p-bromophenyl)-iodonium fluoborate with p-bromoiodobenzene, of di-(p-tolyl)-iodonium fluoborate with p-iodotoluene, of di-(p-anisyl)-iodonium fluoborate with p-iodoanisole, of di-(m-carbethoxyphenyl)-iodonium fluoborate with ethyl m-iodobenzoate, and of di-(m-nitrophenyl)-iodonium fluoborate with m-iodonitrobenzene.

Table 2 gives the conditions of our experiments (reaction temperature and time) and also the degree of exchange and yield of diaryliodonium fluoborates. Due to the fact that the thermal stability of different diaryliodonium fluoborates differs appreciably, we were unable to carry out all the experiments at the same temperature. Therefore, the conclusion drawn from our experiment on the effect of the nature of the substituent in the para or meta position of the benzene ring on the rate of isotopic exchange may be expressed only in the following cautious form: Type II orientants retard the reaction examined. This is apparently caused by reduction of the electron density at the iodine atom in XC_6H_4I molecules, where X is an electronegative substituent. It is natural that the attack on the iodine atom by an aryl cation is hampered.

For unsubstituted phenyl and for those cases where the benzene ring contained a substituent of type I, the reaction formed diaryliodonium fluoborates with quite a high activity. In this connection, the isotopic exchange examined may be recommended as a convenient method of preparing diaryliodonium salts labeled with I^{131}.

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SOLUTION OF BARIUM SULFATE LABELED WITH TWO RADIOACTIVE TRACERS

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The author previously reported [1] that barium sulfate labeled with radioactive sulfur shows a different solubility in water, depending on the specific activity of the salt. In the present work we studied the solution of $B\overset{\times}{a}SO_4$ labeled with Ba^{140} ($T_{1/2}$ = 13 days), and $\overset{\times\ \times}{B}aSO_4$ labeled simultaneously with Ba^{140} and S^{35} ($T_{1/2}$ = = 87.1 days).

The maximum energy of the β-radiation of the radioisotopes present is as follows: Ba^{140}–1.02 Mev and its daughter product La^{140}–2.20 Mev; S^{35}–0.167 Mev [2]. The radiochemical purity of the Ba^{140} and S^{35} was checked by absorption of the β-radiation in aluminum.

TABLE 1

Water-Solubility of Barium Sulfate Labeled with Different Radioactive Tracers at 20 ± 0.5°

Preparation	Specific radioactivity mC/g	Solubility of $BaSO_4$ calculated from tracer, mg/liter
$\overset{\times}{B}aSO_4$	0,7	5,39
$\overset{\times}{B}aSO_4$	0,3	1,28
$B\overset{\times}{a}SO_4$	1,0	41,50
$\overset{\times}{B}aSO_4$	3,3	0,65

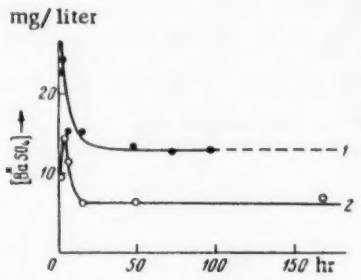

Fig. 1. Kinetics of the solution in water at 20° of $\overset{\times}{B}aSO_4$ preparations of different specific activities: 1) 0.3 mC/g; 2) 3.3 mC/g.

The radioactive preparations of $BaSO_4$ were obtained by mixing hot 0.1 N solutions of $BaCl_2$ and Na_2SO_4, containing appropriate isotopes. The experimental procedure was reported in [1]. The absolute activity of the preparations studied was established by a procedure described in the literature [3]. The solubilities of all the barium sulfate samples were determined by measuring the activity of solution samples after the equilibrium $Ba^{140} \rightarrow La^{140}$ had been established. For samples that simultaneously contained $Ba^{140} \rightarrow La^{140}$ and S^{35}, we used the method of filtering β-radiation of different energies with an aluminum filter [3].

The results of investigating the solution of $\overset{\times}{B}aSO_4$ of different specific activities are presented in Fig. 1.

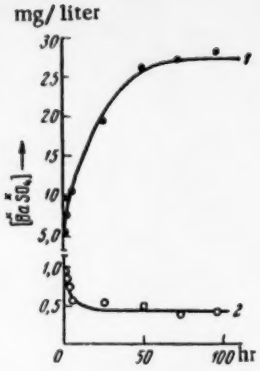

Fig. 2. Kinetics of the solution in water at 20° of $\overset{\times}{Ba}\overset{\times}{S}O_4$ with a specific activity of 3.7 mC/g(Ba^{140}–1.5 mC/g and S^{35}–2.2 mC/g): 1) solubility according to S^{35} radiation; 2) solubility according to Ba^{140} radiation.

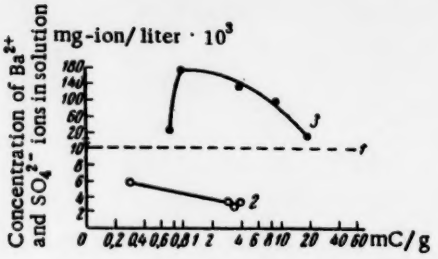

Fig. 3. Relation of the concentration of Ba^{2+} and SO_4^{2-} ions in a saturated $BaSO_4$ solution to the specific radioactivity of the solid phase: 1) concentration of Ba^{2+} and SO_4^{2-} ions corresponding to the normal solubility of the salt; 2) concentration of Ba^{2+} ions during solution of $\overset{\times}{Ba}\overset{\times}{S}O_4$; 3) concentration of SO_4^{2-} ions during solution of $\overset{\times}{Ba}\overset{\times}{S}O_4$.

In the initial period of solution of the $\overset{\times}{Ba}\overset{\times}{S}O_4$ precipitate there was a maximum, which disappeared after 25-hr mixing. More appreciable supersaturation was characteristic of less active salt. We observed an analogous phenomenon for $\overset{\times}{Ba}\overset{\times}{S}O_4$ [1]. The solubility of $\overset{\times}{Ba}\overset{\times}{S}O_4$ in water at 20° was found to be considerably less than reported in the literature [4] for normal barium sulfate (2.3 mg/liter at 18°).

In addition, the solubility of barium sulfate containing Ba^{140} was considerably lower than that of preparations labeled with S^{35} (Table 1).

These observations were confirmed in a study of the solution of barium sulfate labeled with two tracers. Figure 2 presents data on the kinetics of $\overset{\times}{Ba}\overset{\times}{S}O_4$ solution, calculated separately on the activities of Ba^{140} and S^{35}. The results obtained show that a saturated solution of radioactive $\overset{\times}{Ba}\overset{\times}{S}O_4$ contains an excess of SO_4^{2-} ions and a deficiency of Ba^{2+} ions. A similar phenomenon was observed previously [5, 6] during the measurement of electrokinetic potentials of $BaSO_4$. In the given case it was particularly sharply expressed, evidently due to the continuous radiation of electrons by the precipitates we studied.

The facts presented show that radioactive preparations of $BaSO_4$ have a tendency to hold Ba^{2+} ions and repel SO_4^{2-} ions. In the presence of S^{35}, this process develops most strongly with a specific activity of the precipitates of the order of 1 mC/g (Fig. 3). With an increase or a decrease in the specific activity of $\overset{\times}{Ba}\overset{\times}{S}O_4$ there is a decrease in this effect and a change in the concentrations of Ba^{2+} and SO_4^{2-} ions so that the latter approach values corresponding to the normal solubility of inactive $BaSO_4$. The whole complex of phenomena described evidently may be explained by the change in the electrical field of the precipitate under the action of continuous β-irradiation and the associated change in the adsorption properties of the salt and also the absorption of β-particles in the solution.

It may be concluded that the use of radioactive tracers for measuring the solubility of sparingly soluble substances does not guarantee accurate results in all cases. The study of the solubility of cerium oxalate by one of us [7] led to analogous conclusions.

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CONJUGATION OF BONDS IN 1,1-BIS-(TRIFLUOROMETHYL)-2-NITROETHYLENE AND HEXAFLUOROISOPROPYLIDENEMALONIC ESTER

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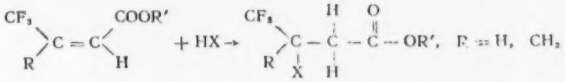
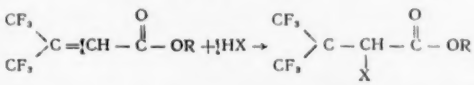
The trifluoromethyl group is one of the strong electron-attracting substituents. The electron-acceptor strength of trifluoromethyl and other negative groups may be compared by studying the order of heterolytic addition of unsymmetrical molecules to carbon–carbon double bonds, polarized by a trifluoromethyl group on one side and by a different negative group on the other. It is known that the addition of nucleophilic and electrophilic reagents to γ, γ, γ-trifluorocrotonic acid or its ester occurs in such a way that the negative part of the molecule added is directed into the β-position with respect to the carboxyl or carbalkoxyl group [1].

A similar order of addition is also observed in the case of the ester of β-methyl-γ, γ, γ-trifluorocrotonic acid [2]:

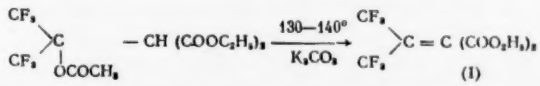


Thus, the carboxyl group is found to be a stronger electron-acceptor group than the trifluoromethyl group.

However, in the case where the carboxyl or carbalkoxyl group is competing with two trifluoromethyl groups, the polarization of the double bond is found to be the reverse; the addition of various reagents to hexafluorodimethylacrylic acid or its ester yields α-substituted derivatives of β,β-bis-(trifluoromethyl)-propionic acid and the effect of the two electron-acceptor trifluoromethyl groups on the polarization of the double bond is found to be stronger than the effect of one carboxyl group [2].



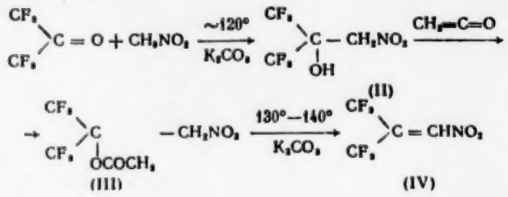
In this connection it seemed to be interesting to determine the competing effect of two trifluoromethyl groups on one side and two carbalkoxyl or one nitro group on the other. We prepared appropriate unsaturated compounds in a study of the reactions of hexafluoroacetone and the further conversions of the substances formed [3]. Low-temperature pyrolysis of β-acetoxyhexafluoroisopropylmalonic ester in the presence of a catalytic amount of potassium carbonate yielded hexafluoroisopropylidenemalonic ester (I).



(I)

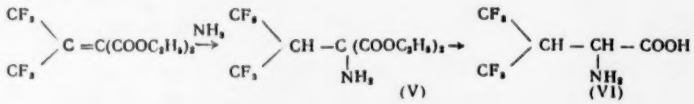
By the reaction of hexafluoroacetone with nitromethane in the presence of potassium carbonate we synthesized 1,1-bis-(trifluoromethyl)-2-nitroethanol (II), which gave the corresponding acetate (III) when treated with ketene.

Distillation of this acetate in the presence of catalytic amounts of potassium carbonate readily formed 1,1-bis-(trifluoromethyl)-2-nitroethylene (IV). The preparation of other fluorinated nitroolefins by this method has already been described in the literature [4].



(III) (IV)

The reaction of hexafluoroisopropylidenemalonic ester with ammonia led to the formation of α-amino-hexafluoroisopropylmalonic ester (V). The structure of this ester was demonstrated by hydrolysis and decarboxylation to previously known [3] hexafluorovaline (VI).

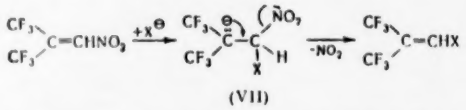


(V) (VI)

An indirect demonstration of the structure of ester (V) was also the ease of hydrolysis of the trifluoromethyl groups in this compound, which was evidently produced by the presence of the hydrogen atom on the carbon atom connected to the trifluoromethyl group (cf. [3]).

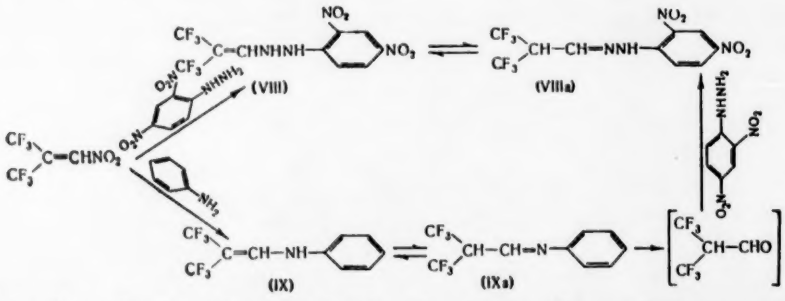
From these data it follows that in the polarization of an olefinic double bond, two trifluoromethyl groups can compete successfully with not only one, but also two carbalkoxyl groups.

In the reaction of 1,1-bis(trifluoromethyl)-2-nitroethylene (IV) with nucleophilic reagents, the order of addition was also the reverse of the usual one. However, the anion (VII) formed was stabilized not only by the addition of a proton, but also by the elimination of a nitrite ion, as occurs in the case of analogous reactions of 1,2-dinitroolefins [6], so that the final result of the reaction was replacement of the nitro group by a new group.



(VII)

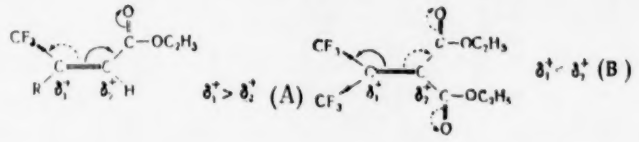
Thus, reactions with 2,4-dinitrophenylhydrazine and with aniline led to the formation of the corresponding substitution products, VIII and IX, respectively, which probably exist in tautomeric forms [the 2,4-dinitrophenylhydrazone of bis-trifluoromethylacetaldehyde (VIIIa) and the anil of bis-trifluoromethylacetaldehyde (IXa)]. Hydrolysis of the anil with dilute HCl and subsequent treatment of the reaction mixture with 2,4-dinitrophenylhydrazine yielded a dinitrophenylhydrazone identical with VIIIa.



(VIII) (VIIIa) (IX) (IXa)

Summarizing the results, it can be stated that the effect of two trifluoromethyl groups attached to one of two carbon atoms, which are connected by a double bond, on the order of addition is found to be greater than might have been expected by simple summing of the effect of each trifluoromethyl group. In actual fact, with one trifluoromethyl group on one side and one carboxyl group on the other side of an olefinic bond, there is a

greater displacement of π-electrons towards the carbalkoxyl group, while two trifluoromethyl groups attract the π-electrons more strongly than two carbalkoxyl groups (see A). This effect evidently occurs due to disruption of the coplanarity of the two voluminous carbalkoxyl groups (see B).



EXPERIMENTAL

Hexafluoroisopropylidenemalonic ester (I). A mixture of 14.5 g of β-acetoxyhexafluoroisopropylmalonic ester [4] and 0.3 g of potassium carbonate in a Claisen flask with a distillation condenser was heated on a bath of Wood's alloy for 2 hr (bath temperature 130-140°). The distillate was washed with saturated sodium carbonate solution and then water and dried with magnesium sulfate. Distillation yielded 10.6 g (87.6% of theoretical) of hexafluoroisopropylidenemalonic ester with b.p. 59-60°/6 mm, $n^{20}D$ 1.3720; d^{20}_4 1.3025; found MR 53.74; calculated for $C_{10}F_6H_{10}O_4$ 52.09.

Found %: C 38.05; 38.25; H 3.05; 3.02; F 36.00; 36.35
$C_{10}F_6H_{10}O_4$. Calculated %: C 38.96; H 3.24; F 37.04

Infrared spectrum: γ^*_{max} 1700 cm^{-1}—absorption of an olefinic bond [6].

Hexafluoroisopropylidenemalonic ester decolorized a neutral aqueous solution of potassium permanganate.

1,1-Bis-(trifluoromethyl)-2-nitroethanol (II). Into a 250-ml steel autoclave were placed 69.0 g of nitromethane and 0.19 g of potassium carbonate. With cooling in dry ice and acetone, 51.9 g of hexafluoroacetone was added. The mixture was heated at 120° for 10-12 hr. Distillation of the unreacted nitromethane yielded 55.1 g (78.4% of theoretical) of 1,1-bis-(trifluoromethyl)-2-nitroethanol with b.p. 67-68°/80 mm, $n^{20}D$ 1.3401; d^{20}_4 1.6597; found MR 28.34; calculated for $C_4F_6H_3O_3N$ 28.65.

Found %: C 21.12; 21.22; H 1.37; 1.43; F 49.46; 48.42; N 6.96; 7.13
$C_4F_6H_3O_3N$. Calculated %: C 21.15; H 1.32; F 50.22; N 6.16

Infrared spectrum: γ_{max} 3400 cm^{-1}—absorption of a hydroxyl group [7]; γ_{max} 1580 cm^{-1}—absorption of a nitro group [7].

Acetate of 1,1-bis-(trifluoromethyl)-2-nitroethanol (III). A large excess of ketene was passed into 9.3 g of 1,1-bis-(trifluoromethyl)-2-nitroethanol at room temperature. Vacuum distillation yielded 8.3 g (75.5% of theoretical) of the acetate with b.p. 60-62°/20 mm, $n^{20}D$ 1.3575; d^{20}_4 1.5368; found MR 38.56; calculated for $C_6F_6H_5O_4$ 39.34.

Found %: C 27.25; 27.33; H 2.00; 2.10; F 40.56; 40.26
$C_6F_6H_5O_4N$. Calculated %: C 26.77; H 1.86; F 42.37

Infrared spectrum: γ_{max} 1580 cm^{-1}—absorption of a nitro group [7]; γ_{max} 1800 cm^{-1}—absorption of an ester group [6].

1,1-Bis-(trifluoromethyl)-2-nitroethylene (IV). A mixture of 20.3 g of the acetate of 1,1-bis-(trifluoromethyl)-2-nitroethanol and 0.03 g of potassium carbonate was placed in a Claisen flask with a distillation condenser and heated on a bath of Wood's alloy for 2 hr (bath temperature 110-140°). The distillate was redistilled (b.p. 70-100°), washed with water, and dried with calcium chloride. Distillation yielded 8.9 g (57% of theoretical) of olefin with b.p. 93-94°, $n^{19}D$ 1.3355; d^{20}_4 1.5637; found MR 26.60; calculated for $C_4F_6HO_2N$ 27.69.

Found %: C 23.20; 23.27; H 0.66; 0.60; F 54.32; 54.67
$C_4F_6HO_2N$. Calculated %: C 22.96; H 0.48; F 54.54

Infrared spectrum: γ_{max} 1700 cm^{-1}—absorption of an olefinic double bond [6].

1,1-Bis-trifluoromethyl-2-nitroethylene was a yellow liquid with a sharp unpleasant smell and was a strong lachrymator; it decolorized a neutral solution of potassium permanganate.

*As in original—Publisher's note.

α-Aminohexafluoroisopropylmalonic ester (V). Into a solution of 7.5 g of hexafluoroisopropylidenemalonic ester in 15 ml of absolute ether was passed 5.7 g of gaseous ammonia. The precipitated ammonium fluoride was removed by filtration, the solvent distilled from the filtrate, and the residue distilled. We obtained 4.2 g (53.1% of theoretical) of α-amonohexafluoroisopropylmalonic ester with b.p. 60-61°/1 mm, $n^{20}D$ 1.3840; d^{20}_4 1.4534; found MR 54.90; calculated for $C_{10}P_6H_{13}O_4N$ 52.20.

Found %	C 37.35; 37.02;	H 4.15; 3.89;	F 37.51; 37.45;	N 4.45; 4.58.	
$C_{10}F_6H_{13}O_4N$. Calculated %	C 36.92;	H 4.00;	F 35.07	N 4.30	

When α-aminohexafluoroisopropylmalonic ester was boiled with excess 25% KOH solution for 7 hr, 63% of the fluorine in the substance was mineralized.

Hexafluorovaline (VI). α-Aminohexafluoroisopropylmalonic ester (0.65 g) was boiled with 2.5 ml of conc. HCl for 7 hr. The reaction mixture was evaporated to dryness, the residue dissolved in absolute alcohol, and a few drops of pyridine added to the solution obtained. We obtained 0.2 g (47.6%) of hexafluorovaline with m.p. 206-207° (decomp.), which did not depress the melting point of an authentic sample [2].

2,4-Dinitrophenylhydrazone of bis-(trifluoromethyl)-acetaldehyde (VIIIa). 1,1-Bis-(trifluoromethyl)-2-nitroethylene (1.3 g) was shaken at room temperature with a solution of 1.3 g of 2,4-dinitrophenylhydrazone in a mixture of 8 ml of conc. H_2SO_4, 40 ml of water, and 5 ml of alcohol.

The precipitate was collected and recrystallized from heptane. The yield was 1.3 g (59% of theoretical). The m.p. was 117-118°.

Found %	C 33.05; 33.05;	H 1.72; 1.75;	F 31.68; 31.25;	N 15.55; 15.65	
$C_{10}F_6H_6O_4N_4$. Calculated %	C 33.34;	H 1.68;	F 31.65;	N 15.56	

Anil of bis-(trifluoromethyl)-acetaldehyde (IXa). 1,1-Bis-(trifluoromethyl)-2-nitroethylene (4.0 g) was dissolved in 3 ml of absolute ether and 1.78 g of aniline added slowly with cooling in dry ice and acetone; the temperature of the mixture was slowly raised to room temperature, when there was a vigorous evolution of nitrogen oxides. For completion of the reaction, the solution was boiled under reflux on a water bath for 30 min. Washing with water, drying with calcium chloride, removal of the solvent, and vacuum distillation yielded 2.9 g (60.4% of theoretical) of a Schiff's base with b.p. 81-82°/5 mm, $n^{20}D$ 1.4781; d^{20}_4 1.4016.

Found %	C 86.68; 46.76;	H 2.76; 2.78;	F 43.02; 42.65;	N 6.01; 6.10	
$C_{10}F_6H_7N$. Calculated %	C 47.05;	H 2.74;	F 44.70;	N 5.49	

Treatment of the anil obtained with 2,4-dinitrophenylhydrazine in the presence of conc. HCl formed the hydrazone VIIIa with m.p. 117-118°, which did not depress the melting point of an authentic sample.

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MECHANISM OF ISOMERIZATION AND DEUTERIUM EXCHANGE OF NAPHTHENES IN LIQUID HBr

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The rate of the isotopic exchange of hydrogen in cyclohexane with liquid DBr, catalyzed by $AlBr_3$, was measured in previous work [1]. By measurement of the Raman spectra, it was established that the cyclohexane was isomerized to methylcyclopentane. In a development of this investigation, we obtained the results given below on the kinetics of the isomerization of methylcyclopentane and hydrogen exchange in a series of naphthene hydrocarbons dissolved in liquid hydrogen bromide enriched in deuterium (as DBr).

The observations made led to the conclusion that carbonium ions may participate in these reactions, and this is of importance in the interpretation of their mechanism. Cyclopentane, methylcyclopentane, cyclohexane, and methylcyclohexane of high purity were chromatographed on a column packed with silica gel and dried with metallic sodium. They did not give a formalite reaction. $AlBr_3$ and $GaBr_3$, which were synthesized from the elements, were purified carefully and samples of them were taken without contact with atmospheric moisture by a method which was developed specially [2]. The experiments with solutions in liquid DBr were carried out by the procedure in [3] with a few modifications. Measures were taken to reduce to a minimum the impurities (unsaturated hydrocarbons, moisture, bromine, and oxygen) which could affect the course of the isomerization.

In the determination of the isomerization rate of methylcyclopentane, the composition of the reaction mixture was established by measurement of the refractive index with the use of a calibration curve. At equilibrium (25°), the isomerizate contained 12.5 mol. percent of methylcyclopentane. The isomerization rate constant $\underline{k}$ was calculated from an equation of the first order (sec^{-1}). It was proportional to the catalyst concentration C (in moles per mole of liquid HBr): $k^* = k/C = const$. In experiments with $AlBr_3$, C varied from $1.4 \cdot 10^{-3}$ to $6.9 \cdot 10^{-3}$ and we obtained the following values of $k \cdot 10^4/C \cdot 10^3$: 1.0; 1.4; 1.5; 1.3; 1.6; 1.8; 1.3; 0.8; 1.1; 1.1; 1.0; 1.2; mean 1.2. In experiments with $GaBr_3$, C varied from $1.7 \cdot 10^{-3}$ to $4.8 \cdot 10^{-3}$. The values of $k \cdot 10^4/C \cdot 10^3$ were 0.2, 0.1, 0.2, and 0.2; mean 0.2. Consequently, $AlBr_3$ was found to be approximately six times more active than $GaBr_3$. When 0.03 g of cyclohexyl bromide was added to 0.3 g of methylcyclopentane, the isomerization catalyzed by $AlBr_3$ was increased: $k \cdot 10^4/C \cdot 10^3$: 10, 9, 9, mean 9.

In the presence of $AlBr_3$, solutions of cyclopentane, methylcyclopentane, and cyclohexane in liquid HBr were first colorless and then gradually became yellow; the intensity of the color depended both on the $AlBr_3$ concentration and on the duration of the experiment. After 15-20 hr, solutions of cyclohexane and methylcyclopentane with $C = (2\text{-}3) \cdot 10^{-2}$ mole of $AlBr_3$ per mole of HBr deposited a yellow–orange oil. A solution of cyclopentane began to form layers after 6 hr at 25° with $C = 1.4 \cdot 10^{-2}$. All experiments on isomerization and deuterium exchange were carried out in homogeneous solutions. A solution of methylcyclohexane with $AlBr_3$ added remained colorless and homogeneous even after several days. During the experiments, the refractive indices of cyclopentane and methylcyclohexane did not change within the accuracy of measurements on an Abbe type refractometer. An isomerizate of equilibrium composition was obtained after experiments with methylcyclopentane and cyclohexane.

The deuterium exchange rate was measured at 25°. The results were calculated in the same way as in [1]. Over the range of concentrations C = (0.2-1.3) · 10^{-2} moles $AlBr_3$/ mole HBr, the rate constants of deuterium exchange $\underline{k}$ (sec^{-1}) were approximately proportional to C. We present the relative rate constants $k' = k \cdot 10^5/C \cdot 10^2$.•

Cyclopentane: 5, 6, 5, 7, 4, 5, 6, 8, mean 5.

Methylcyclopentane: 1.4, 1.4, 1.6, 0.6, 1.6, mean 1.3.

Cyclohexane: 0.5, 0.4, 0.6, 0.6, 1.8, 1.6, 2.4, 0.7, 1.5, 1.2, 1.3, 0.6, 0.6, 1.9, 1.9, 2.1, 2.3, 2.8, 2.6, mean 1.4.

Methylcyclohexane: 3, 3, 4, 4, mean 3.6.

Isotopic exchange of hydrogen in methylcyclopentane proceeds at a rate which is two orders less than the rate of isomerization. Consequently, regardless of whether the starting material was methylcyclopentane or cyclohexane, the exchange reaction actually occurred in the equilibrium mixture of these hydrocarbons (equilibrium constant $k_{27°} = 7.6$ [4]).

To elucidate the mechanism of deuterium exchange, we carried out experiments in which cyclopentyl bromide or cyclopentene was added to cyclopentane in an amount corresponding to 0.1 mole per mole of hydrocarbon; cyclohexyl bromide or cyclohexene were added to cyclohexane or methylcyclohexane. We obtained the following values for $k'_1 = k \cdot 10^5/C \cdot 10^2$. Experiments with bromide added are marked with a star.

Cyclopentane: 35, 52, 39, 25, 46•, 50•, mean 40.

Cyclohexane: 4, 4, 6, 4, 5•, 7•, mean 5.

Methylcyclohexane: 7•, 10•, mean 8.5.

Let us compare the relative values of the rate constants of deuterium exchange in experiments with additives and without them:

Hydrocarbon	k'_1	k'	$k'_1 : k'$
Cyclopentane	40	5	8
Methylcyclopentane	–	1.3	–
Cyclohexane	5	1.4	3.5
Methylcyclohexane	9	3.6	2.6

It should be noted that the introduction of a halogen derivative or an unsaturated hydrocarbon into the reaction mixture not only increased the deuterium exchange rate severalfold, but also intensified the color of cyclopentane solutions and promoted the precipitation of oil in cyclohexane•• and methylcyclohexane solutions. This may be explained by autocondensation of the saturated hydrocarbon, which occurs in the presence of the halogen derivative with $AlBr_3$ as catalyst and, according to Nenitzescu [5], proceeds through the formation of a carbonium ion and the elimination of H^- from the saturated hydrocarbon. The hydrogen in cyclohexyl bromide is quite rapidly exchanged for deuterium of liquid DBr when $AlBr_3$ is added. This may be compared with the observations of G. A. Razuvaev and his co-workers [6], according to whom deuterium exchange occurs between deuterocyclohexane and cyclohexyl chloride at 18° with $AlCl_3$ as catalyst.

DISCUSSION OF RESULTS

A careful study of the isomerization of saturated hydrocarbons, in particular, methylcyclopentane, showed [7-9] that $AlBr_3$ (or $AlCl_3$) does not catalyze it in the absence of a promoter and that the reaction does not proceed when HBr (or HCl) is added. The presence of traces of olefin in the system are also necessary. Alkyl halide is

•When samples of $AlBr_3$ were taken without the use of the procedure described in [2], the rate constants obtained were less by a factor of approximately two.

••In one experiment the oil had the following constants: b.p. 213-215°; $n^{20}D$ 1.5133. The properties and composition of the oil were not studied in more detail.

then obtained (it may also be added directly) and its subsequent reaction with $AlBr_3$ produces carbonium ions according to the equation

$$RBr + ArBr_3 \rightarrow R^+AlBr_4^-, \quad (I)$$

and these initiate a chain isomerization reaction. However, as we demonstrated, in the case where hydrogen bromide is not the additive, but the solvent, $AlBr_3$ and $GaBr_3$ isomerize methylcyclopentane to cyclohexane (in the absence of activator) in the pure state and the addition of cyclohexyl bromide only accelerates the reaction, whose rate at 25° is considerable without it.

Initiation of isomerization by the formation of carbonium ions according to equation (I) is also realized if the catalyst is an aluminum halide promoted by water. In the opinion of Nenitzescu [5], carbonium ions then arise due to elimination of hydrogen from the saturated hydrocarbon in the form of the hydride ion (H^-), which, being unable to exist independently, immediately combines with a proton of the aluminum halide hydrate (a strong complex hydrogen acid) to form molecular hydrogen, i.e., the reaction is schematically represented by the equation:•

$$\equiv C - H + H^+ \rightarrow \equiv C^+ + H_2. \quad (II)$$

Nenitzescu actually detected the formation of molecular hydrogen in the isomerization of methylcyclopentane. Solutions of $GaBr_3$ and $AlBr_3$ in liquid HBr are very strong acids (see [10], p. 63) and it is possible that Nenitzescu's mechanism applies to isomerization under these conditions. We have no direct experimental data on the formation of molecular hydrogen.

Let us now examine the results obtained on deuterium exchange in naphthene hydrocarbons. Beginning with Ingold, many authors (Burwell, Beeck and Stevenson, D. N. Kursanov and V. N. Setkina, et al. [10, 11]) studied the isotopic exchange of hydrogen in saturated hydrocarbons with deuterosulfuric acid and established that hydrocarbons with a tertiary carbon atom participate in exchange reactions. It has been suggested and become generally accepted that sulfuric acid oxidizes the hydrogen atom of the methyne group and the carbonium ions thus produced initiate a chain deuterium-exchange reaction.

In the deuterium exchange of naphthenes with a solution of $AlBr_3$ in liquid DBr discussed here, as in deuterium exchange with liquid DF [12], the oxidation stage is excluded and therefore the mechanism proposed for hydrogen exchange with sulfuric acid is inapplicable.•• D. N. Kursanov reported that this limitation may be avoided if, following Whitmore and Nenitzescu, it is assumed that carbonium ions are formed in hydrogen halide solutions according to equation (II).

We consider it probable that carbonium ions participate in the exchange reaction with a saturated hydrocarbon catalyzed by $AlBr_3$ in liquid HBr, as the addition of the halogen derivative to the naphthene hydrocarbon considerably accelerates the exchange and this is logically connected with the formation of carbonium ions according to equation (I). More accurately speaking, in a solvent with a low dielectric constant such as liquid HBr ($DC_{25} = 4$), one can hardly expect the formation of free ions and it is more likely that the C-Br bond is polarized under the action of $AlBr_3$

$$R - Br + AlBr_3 \rightarrow \overset{\delta+}{R} - \overset{\delta-}{Br} \cdot AlBr_3 \quad (V)$$

and such a polarized complex participates in the transition state. In the absence of the halogen derivative of the hydrocarbon, "carbonium ions" may appear analogously as was assumed above in the discussion of isomerization

•There are other known reactions of the acid–base type in which molecular hydrogen and a hydride ion participate:

$$\equiv CH + H^- \rightarrow \equiv C^- + H_2 \quad (III)$$

i.e., a reaction between a hydrocarbon and a hydride with the formation of a carbanion and hydrogen:

$$\equiv C^- + H_2 \rightarrow \equiv CH + H^- \quad (IV)$$

i.e., a reaction between a carbanion and molecular hydrogen in which a hydrocarbon and a hydride are formed (see [10], p. 113).

••It is obvious that it is not essential that a tertiary carbon atom should be present in the molecule of the saturated hydrocarbon as exchange of hydrogen occurs in the cyclopentane molecule, whose constants do not change during the exchange reaction.

of methylcyclopentane in liquid HBr without promoter. The detailed mechanisms of the isomerization and deuterium-exchange processes are different, as follows from the different rates of these reactions.

The opinions presented, whose hypothetical character should be emphasized, make it possible to use a single approach to the three reactions which occur simultaneously in liquid DBr (isomerization, deuterium exchange, and condensation). Moreover, they eliminate the discrepancy between existing ideas on the mechanisms of deuterium exchange in saturated hydrocarbons with sulfuric acid and with liquid hydrogen halides.

Ingold considered that the sole method by which sulfuric acid may participate in the isotopic exchange of hydrogen is by the donation of a proton (or deuteron). It is possible that the oxidizing action of sulfuric acid plays a definite role in exchange reactions, but obviously its high acidity is of prime importance. It cannot be by chance that there is a linear relation between the exchange rate and the acidity function of the sulfuric acid acid and no relation between the exchange rate and the degree of oxidation of the hydrocarbon ([10], p. 236). All isotopic exchanges of hydrogen in saturated hydrocarbons are characterized by the fact that they can be realized only with the aid of the strongest acids because saturated hydrocarbons are some of the weakest bases among hydrocarbons, as also follows from the conception of the acid–base nature of hydrogen exchange.

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ROUTES FOR BUILDING THE BA RING SYSTEM OF TETRACYCLINES

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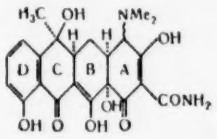
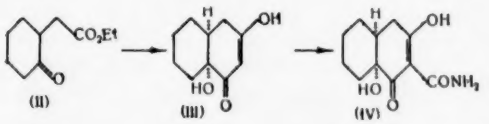
We previously [1] described the synthesis of ketols of the hydroanthracene series, two rings of which were similar in structure to rings D and C of tetracycline (I), while the third ring, corresponding to ring B, contained functional groupings making it possible to build up ring A of tetracyclines.



(I)

Before undertaking the next stage, i.e., the construction of the fourth ring, we studied possible routes to this on simpler examples, namely, cyclohexane derivatives. Ethynylation of cyclohexanone-2-acetic ester (II) with subsequent hydration of the triple bond and cyclization of the hydroxy keto ester yielded cis-decalol-9-dione-1,3 (III) and carboxamidation of this led to cis-2-carboxamidodecalol-9-dione-1,3 (IV), the right-hand ring of which contains all the functional groupings of ring A of tetracyclines, with the exception of the dimethylamino group [2].

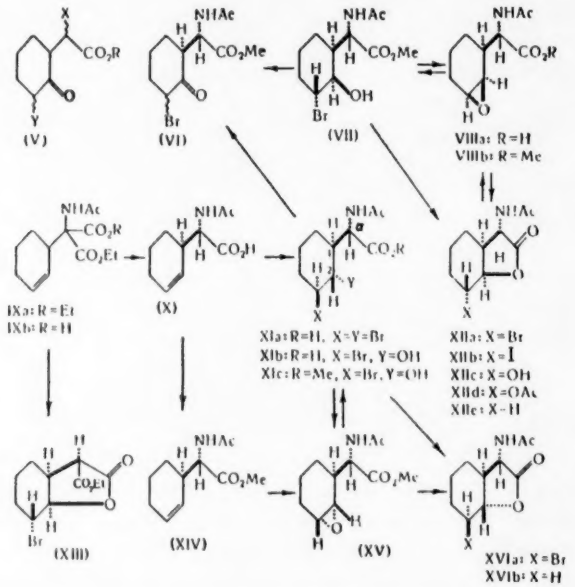


(II) (III) (IV)

The purpose of the present work was to study the possibility of constructing the complete BA ring system of tetracyclines. On the basis of the results of previous investigations it seemed expedient to study first routes for synthesizing compounds of type (V), where X is an acylated amino group and Y a substituent which may be converted to a carboxyl group at later stages in the synthesis. This type of key compound could be a basis for the subsequent construction of the complete BA ring system of tetracycline (I). As a model substance for the synthesis of compounds of type (V) we took 1,2-dibromocyclohexane so that for the construction of the tetracyclic system DCBA it is possible to use the dibromide of the tricyclic ketol we described previously [1]. As the first representative of compounds of type (V) we synthesized the methyl ester of 3-bromo-2-ketocyclohexylaceturic acid (VI).

Condensation of 1,2-dibromocyclohexane with acetaminomalonic ester in the presence of two moles of sodium ethylate [3] gave a 52% yield of 2-cyclohexenylacetaminomalonic ester (IXa). The same compound was obtained in 62% yield by condensation of acetaminomalonic ester with 3-bromocyclohexene in the presence of one mole of sodium ethylate. Hydrolysis of the diester (XIa) with one equivalent of a 1 N solution of potassium hydroxide in methanol at room temperature led to a 70% yield of the acid ester of 2-cyclohexenylacetaminomalonic acid (IXb), while hydrolysis of diester (XIa) under the same conditions with two equivalents of potassium hydroxide gave a 97% yield of 2-cyclohexenylaceturic acid (X).

Bromination of the acid ester (IXb) in chloroform at -10° led to the carbethoxy bromo lactone (XIII) and hydrolysis of this with subsequent decarboxylation formed the bromo lactone (XIIa). Bromination of 2-cyclohexenylaceturic acid (X) in acetic acid at 5-10° yielded the bromo lactone (XIIa) (37% yield) and the dibromo acid (XIa) (35% yield). It was subsequently found to be more convenient to brominate 2-cyclohexenylaceturic acid (X) in an aqueous solution of sodium carbonate [4, 5]. Under these conditions we obtained the bromo lactone (XIIa) and the bromo hydroxy acid (XIb) in yields of 52 and 36%, respectively. Iodolactonization [6] of the acid (X) in an aqueous solution of sodium bicarbonate gave a 98% yield of the iodo lactone (XIIb).



We used the bromo hydroxy acid (XIb), the bromo lactone (XIIa), and the iodo lactone (XIIb) for preparing the bromo keto ester (VI).

Methylation of the bromo hydroxy acid (XIb) with diazomethane in dioxane gave the methyl ester of the bromo hydroxy acid (XIc). This ester was also synthesized by another method. The action of methyl iodide on the silver salt of 2-cyclohexenylaceturic acid (X) yielded its methyl ester (XIV), which was oxidized with perbenzoic acid to the α-oxide (XV), and the latter was heated with pyridine hydrobromide in absolute ethanol to give the methyl ester of the bromo hydroxy acid (XIc). Oxidation of this with chromic oxide in 80% acetic acid at room temperature gave a 78% yield of the methyl ester of the bromo keto acid (VI). We obtained the same bromo keto ester in the following way. The action of one equivalent of a 0.5 N solution of potassium hydroxide in absolute methanol at room temperature on the bromo lactone (XIIa) or the iodo lactone (XIIb) gave an almost quantitative yield of the methyl ester of the β-oxido acid (VIIIb). When the latter was heated with pyridine hydrobromide in absolute ethanol, it was converted into the ester of the bromo hydroxy acid (VII), which was the stereoisomer of the ester (XIc). Oxidation of the ester of the bromo hydroxy acid (VII) with chromic oxide in acetic acid led to the bromo keto ester (VI) (74% yield).

The structure of the compounds obtained was established in the following way. Lactonization of the bromo hydroxy acid (XIb) by boiling in 0.1 N sulfuric acid gave a 78% yield of the bromo lactone (XVIa), which was catalytically halogenated over palladium oxide or Raney nickel in the presence of diethylamine to yield the

Compound	M.p., °C	Solvent	Found, %				Calculated, %			
			C	H	N	Br (I)	C	H	N	Br (I)
VI	134—135	AcOEt	43,02	5,34	4,41	26,83	43,15	5,27	4,57	26,10
VII	137—138	20% EtOH	43,18	5,86	4,37	25,71	42,87	5,89	4,55	25,93
VIIIb	100—101	C_6H_6-hexane	58,32	7,76	6,21	—	58,13	7,54	6,16	—
IXa	48—49	Et_2O	60,37	7,97	4,68	—	60,59	7,80	4,71	—
IXb	116—117	20% EtOH	58,02	7,27	5,29	—	57,98	7,11	5,20	—
X	178—179	EtOH	60,58	7,58	7,24	—	60,89	7,67	7,10	—
XIa	167—168	20% EtOH	33,76	4,28	3,87	44,31	33,63	4,23	3,92	44,76
XIb	168—169	20% EtOH	40,69	5,38	4,82	27,36	40,83	5,48	4,76	27,17
XIc	134—135	AcOEt-heptane	43,13	5,98	4,58	25,83	42,87	5,89	4,55	25,93
XIIa	178—179	20% EtOH	43,53	5,20	5,02	29,11	43,49	5,11	5,07	28,97
XIIb	163—164	H_2O	37,12	4,42	4,29	39,23	37,17	4,37	4,33	39,28
XIIc	192—193	AcOEt	56,43	7,15	6,68	—	56,32	7,09	6,57	—
XIId	129—130	C_6H_6-hexane	56,52	6,65	5,51	—	56,46	6,71	5,49	—
XIIe	174—175	AcOEt	60,61	7,58	6,85	—	60,89	7,67	7,10	—
XIII	138—139	20% EtOH	44,76	5,08	4,03	22,80	44,83	5,21	4,04	22,95
XIV	102—103	C_6H_6-hexane	62,61	8,27	6,44	—	62,54	8,11	6,63	—
XV	100	C_6H_6 hexane	58,42	7,60	6,02	—	58,13	7,54	6,16	—
XVIa	172—173	20% EtOH	43,36	5,17	4,68	28,82	43,49	5,11	5,07	28,97
XVIa	148—149	AcOEt	60,91	7,57	6,74	—	60,89	7,67	7,10	—

lactone of threo-trans-2-hydroxycyclohexylaceturic acid (XVIb) and this was obtained in its turn by acetylation of the lactone of threo-trans-2-hydroxycyclohexylglycine, which has been described previously [7]. Thus, with respect to the asymmetric centers C_α and C_1, the bromo hydroxy acid (XIb) belongs to the threo series, in which the hydroxyl group at C_2 is in the trans position with respect to the N-acetylglycine residue.

An investigation of the infrared spectrum of the bromolactone (XIIa) showed that it is a γ-lactone (ν_{CO} = 1793 cm^{-1}). The cis coupling of the lactone and cyclohexane rings in (XIIa) and (XIIb) was established on the basis of the following data. Catalytic dehalogenation of the bromo lactone (XIIa) and the iodo lactone (XIIb) gave the same lactone, isomeric with the lactone of threo-trans-2-hydroxycyclohexylaceturic acid (XVIb). As the formation of these two halo lactones occurred under conditions under which there should be no epimerization [4, 8], both of them, like the bromo hydroxy acid (XIb) should belong to the threo series with respect to the centers C_α and C_1. Consequently, the lactone formed by catalytic dehalogenation of the halo lactones (XIIa) and (XIIb) should also have a threo configuration, differing from the isomeric lactone (XVIb) only in the configuration of the asymmetric center C_2 so that it can be assigned the structure of the lactone of threo-cis-2-hydroxycyclohexylaceturic acid (XIIe).

The structure of the methyl ester of the β-hydroxy acid (VIIIb) was established in the following way. Its hydrolysis by 10% aqueous potassium hydroxide at room temperature yielded the oxido acid (VIIIa) and the action of 1 N sulfuric acid on the latter (20°, 12 hr) led to the hydroxy lactone (XIIc). The same compound was formed in 38% yield by hydroxylation of 2-cyclohexenylaceturic acid (X) with performic acid. The cis coupling of the lactone and cyclohexane rings in (XIIa) was caused by the β-configuration of the oxide (VIIIb.)

In the ester of the bromo hydroxy acid (VII) obtained from the β-oxido ester (VIIIb), the hydroxyl group at C_2 was in the cis position relative to the aceturic acid residue as the action of a 10% solution of hydrogen bromide in acetic acid on ester (VII) formed the bromo lactone (XIIa). The formation of the same bromo keto ester (VI) by oxidation of the stereoisomeric bromo hydroxy esters (XIc) and (VII) is additional confirmation of the structures of the latter.

The bromo keto ester (VI), hydroxy lactone (XIIc) and its acetate (XIId) [synthesized from (XIIc) by the action of acetic anhydride in pyridine], and also the stereoisomeric oxide esters (VIIIb) and (XV) may be used for building up the BA ring system of tetracyclines.

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CATALYTIC DEHYDROCYCLIZATION OF β-n-BUTYLNAPHTHALENE

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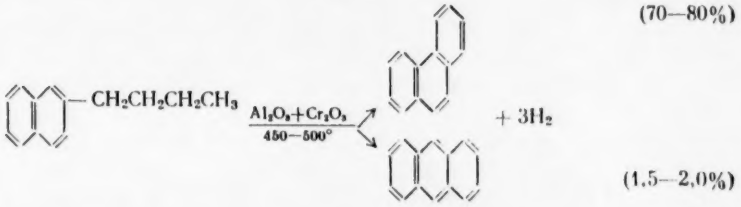
In the development of the first investigations of the catalytic dehydrocyclization of alkanes on oxide catalysts, a series of authors have shown the cyclization reaction can be carried out not only with free alkane molecules, but also with side chains on a benzene nucleus with not less than four carbon atoms. First B. L. Modavskii et al. [1] and then S. S. Nametkin, M. I. Khotimskaya, and L. M. Rozenberg [2] observed the formation of naphthalene in an investigation of the conversion of n-butylbenzene on dehydrogenating catalysts. S. R. Sergienko [3] obtained β-methylnaphthalene as a result of dehydrocyclization of isoamylbenzene. One of us recently showed that normal high-molecular alkanes, for example, hexa-, hepta-, and octadecane, also undergo dehydrocyclization under certain conditions with the formation of condensed systems, namely, naphthalene, phenanthrene, benzanthracene, and chrysene [4, 5].

In the present work we achieved the dehydrocyclization of β-n-butylnaphthalene to phenanthrene and anthracene. A detailed investigation of the composition of the catalyzates obtained showed that under conditions we adopted, cyclization proceeds through the α-carbon atom of the naphthalene nucleus closest to the butyl group with the predominant formation of phenanthrene.



The dehydrocyclization experiments were carried out in a normal flow apparatus in a hydrogen atmosphere at 400, 450, 500, and 550° and a hydrocarbon input space velocity of 0.1 to 1.0 hr^{-1} in the presence of an aluminum—chromium catalyst containing 20% of chromium oxide. The catalyst was prepared by coprecipitation of aluminum and chromium hydroxides from molar solutions of their nitrates with excess ammonia solution. The catalyst was formed and dried at 120° and then before experiments it was treated with hydrogen in a catalytic tube with the temperature gradually raised to 500°. After each experiment, the catalyst was regenerated in the usual way with successive oxidation with air and treatment with hydrogen. The starting β-n-butylnaphthalene was prepared by the Friedel—Crafts reaction by the reaction of naphthalene with butyryl chloride in nitrobenzene in the presence of aluminum chloride [6] and subsequent reduction of the n-propyl β-naphthyl ketone formed by a modification of the Wolff—Kizhner method [7]. The pure β-n-butylnaphthalene had the following properties: b.p. 136-137°/7 mm, $n^{20}D$ 1.5780, d^{20}_4 0.9669. Literature data [6]: b.p. 292°/760 mm, $n^{20}D$ 1.5776, d^{20}_4 0.966.

TABLE 1

Results of Dehydrocyclization of β-n-Butylnaphthalene in the Presence of an Aluminum–Chromium Catalyst

Expt. No.	Temp., °C	Space velocity, hr^{-1}	β-n-Butylnaphthalene passed, g	Catalyzate composition					Gaseous reaction products at s.t.p., liters
				total		liquid portion, wt., %	phenanthrene, wt., %	anthracene, wt. %	
				g	wt. %				
1	452	0,12	22,3	17,1	76,7	4,2	92,4	2,6	6,1
2	450	0,21	23,2	17,6	76,0	12,3	82,6	—	7,0
3	450	0,20	22,9	17,5	76,3				
4	451	0,38	22,9	18,1	78,9	43,9	55,8	—	4,2
5	452	0,60	23,2	19,1	82,2	49,0	50,0	—	Not det.
6	448	1,0	22,2	20,4	92,0	85,8	14,2	—	2,0
7	400	0,38	23,2	19,5	84,4	85,5	13,3	—	Not det.
8	500	0,38	23,2	19,1	82,5	5,0	93,4	1,6	5,3
9	550	0,38	23,2	17,9	79,1	5,0	94,1	0,8	6,2

The results of dehydrocyclization experiments are presented in Table 1.

The content of cyclization products in catalyzates from experiments with a space velocity of 0.38 hr^{-1} at 400° was 13.3%; at 450°, 55.8%; and at 500 and 580°, 95%. The catalyzate obtained at 450° and a space velocity of 0.1 hr^{-1} also contained 95% of cyclization products. An increase in the space velocity by a factor of 10 at the same temperature led to a fall in the cyclization product content of the catalyzate to 14.2%. The cyclization products consisted predominantly of phenanthrene. Anthracene in amounts of 1 to 3% was isolated from catalyzates from experiments at 500 and 550° and a space velocity of 0.38 hr^{-1}, and at 450° and a space velocity of 0.1 hr^{-1}. In other experiments, anthracene was detected only as traces from the formation of a band with a blue fluorescence in ultraviolet light during chromatography of the cyclization products on alumina.

The catalyzates were analyzed in the following way. The liquid portion of the catalyzates was separated from the solid by filtration and vacuum distilled; the crystalline residue thus obtained was added to the solid portion of the catalyzate. The crystalline part of the catalyzate was treated with ether in the cold. Removal of the ether in a flask left "crude" phenanthrene (m.p. 96-98°), containing a very small amount of anthracene, which is sparingly soluble in ether. For further purification of the phenanthrene, a solution of it in hexane was passed through an alumina column with subsequent elution with a mixture of hexane and benzene (1 : 1). The elution was followed by examining the column under a quartz lamp. After purification, the phenanthrene melted at 99.5-100°. The ether-insoluble portion of the catalyzate was anthracene with m.p. 216-216.5° (after chromatography on alumina). The liquid portions of the catalyzate from each experiment were combined and distilled on a vacuum column. As analysis showed, it consisted mainly of unchanged β-n-butylnaphthalene. Distillation of 32 g of the combined liquid portions of the catalyzates from experiments 1-6, which were carried out at 450°, gave 19.2 g of starting hydrocarbon (b.p. 115-116°/3 mm, $n^{20}D$ 1.5782, d^{20}_4 0.9670), 0.65 g (0.6% of the butylnaphthalene passed) of naphthalene (as a sublimate), and 4.2 g (3.8%) of fractions boiling below β-n-butylnaphthalene: 2.1 g with b.p. 119-121°/10 mm, $n^{20}D$ 1.6012, d^{20}_4 0.9873; and 2.1 g with b.p. 141°/10 mm, n^{20} 1.5892. These fractions were apparently lower alkylnaphthalenes, formed as a result of cracking of β-n-butylnaphthalene. The gaseous reaction products formed in experiments at 450° contained, apart from hydrogen, a small amount of cracking products: 0.5-0.9% of unsaturated and 6-7% of saturated hydrocarbons. Thus, as these data show, cracking did not play an important part under the conditions we adopted.

The work shows that in the presence of aluminum–chromium catalyst, β-n-butylnaphthalene readily undergoes dehydrocyclization predominantly at the α-carbon atom with the formation of phenanthrene. The phenanthrene yields at 450° and a butylnaphthalene input space velocity of 0.1 hr^{-1} and also at 500° and a space velocity of 0.4 hr^{-1} reached 70-80% of theoretical. Under these conditions the anthracene yields did not exceed 1.5-2%.

At the present time work is continuing on the dehydrocyclization of other β- and also α-alkylnaphthalenes.

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DIMETHYLGLYOXIMATES OF TRIVALENT COBALT CONTAINING A SELENOCYANATE GROUP

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There are a large number of complex compounds of trivalent cobalt with dimethylglyoxime containing a thiocyanate group, for example $[CoPy(DH)_2(NCS)]$• [1], and $H[Co(DH)_2(NCS)_2]$ [2]. Dimethylglyoximates of cobalt with thiourea have also been synthesized [3].

X-ray structural investigations showed that thiourea and ethylenethiourea in the products of addition to salts of nickel [4], cadmium [5, 6], etc. are bound to the metal atom through sulfur. There is no doubt that in cobalt dimethylglyoximates containing thiourea the bond is formed in the same way. Due to the great similarity in the behavior of cobalt dimethylglyoximates including thiourea in the inner sphere and the behavior of dimethylglyoximates containing a thiocyanate group, it can be assumed with a considerable degree of probability that in cobalt dimethylglyoximates, the thiocyanate group is also connected to the cobalt atom through sulfur.

The selenocyanate ion is very similar to the thiocyanate ion. In particular, various complex selenocyanates are known (see, for example, [7-9]). It seemed interesting to determine the possibility of introducing a selenocyanate ion into the inner sphere of cobalt dimethylglyoximates.

A solution of potassium selenocyanate reacts very readily with trans-chloro-bis-dimethylglyoximatoaquocobalt [10, 11] to form fine brown-red crystals of potassium diselenocyanato-bis-dimethylglyoximatocobaltiate $K[Co(DH)_2(SeCN)_2]$.

The ion $[Co(DH)_2(SeCN)_2]^-$ is very similar to the dithiocyanato-bis-dimethylglyoximatocobaltiate ion [2]. Both give sparingly soluble colored salts with various metals. With a slight rise in pH, aqueous solutions of these ions form precipitates of thiocyanato- and selenocyanato-bis-dimethylglyoximatoaquocobalt, respectively. The action of one mole of an organic amine on an aqueous alcohol solution of the diselenocyanato-bis-dimethylglyoximatocobaltiate ion eliminates one selenocyanato group with the formation of compounds of the type $[CoAmine(DH)_2(SeCN)]$. A similar reaction is shown by the dithiocyanato-bis-dimethylglyoximatocobaltiate ion.

Thiocyanate and selenocyanate ions behave very similarly toward nitro-bis-dimethylglyoximatoaquocobalt [12]. Heating equimolecular amounts of nitro-bis-dimethylglyoximatoaquocobalt and potassium selenocyanate forms the selenocyanatonitro-bis-dimethylglyoximatocobaltiate ion $[Co(DH)_2(NO_2)(SeCN)]$. Its formation was demonstrated by its precipitation as the salt $\{CoPy_2(DH)_2[Co(DH)_2(NO_2)(SeCN)]\}$ .Like the thiocyanatonitro-bis-dimethylglyoximatocobaltiate ion [12], the selenocyanato-bis-dimethylglyoximatocobaltiate ion loses a nitro

•DH represents the dimethylglyoxime residue $CH_3-\underset{\underset{-ON}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-CH_3$.

group in a slightly alkaline medium and is converted into the selenocyanato aquo compound. This indicates that in cobalt dimethylglyoximates, the selenocyanate group, like the thiocyanate group, has a greater trans effect than the nitro group.

We should mention in particular the exceptional stability of the diselenocyanato-bis-dimethylglyoximatocobaltiate ion toward acids. This is all the more interesting as the free selenocyanate ion is exceptionally unstable in the presence of hydrogen ions. This may indicate that the selenocyanate group in the dimethylglyoximates is connected to cobalt through the selenium.

Like thiourea, selenourea tends to form complexes with salts of heavy metals [13, 14]. We found that selenourea may be introduced into the inner sphere of cobalt dimethylglyoximates. Thus, chloro-bis-dimethylglyoximatoselenocarbamidecobalt was obtained very readily by the action of selenourea on chloro-bis-dimethylglyoximatoaquocobalt.

EXPERIMENTAL

Potassium diselenocyanato-bis-dimethylglyoximatocobaltiate $K[Co(DH)_2(SeCN)_2]$. Trans-chloro-bis-dimethylglyoximatoaquocobalt $CoH_2O(DH)_2Cl$• (1.7 g, 5 mmole) was covered with 75 ml of hot 50% alcohol and a solution of 1.44 g (10 mmole) of potassium selenocyanate in 25 ml of alcohol added. When heated on a water bath for a few minutes, the gray-green chloro aquo compound changed to a red-brown crystalline mass, which was collected on a glass filter and washed with water, alcohol, and ether. The yield was 60-70% of theoretical. The crystals appeared as fine yellow platelets under a microscope.

$K[Co(C_4H_7O_2N_2)_2(CNSe)_2]$. Found %: Co 10.85; 10.97; Se 29.10; 29.28; 29.12
Calculated %: Co 10.93;

Ammonium diselenocyanato-bis-dimethylglyoximatocobaltiate $NH_4[Co(DH)_2(SeCN)_2]$. A mixture of 1.7 g of trans-chlorobisdimethylglyoximatoaquocobalt and 1.44 g of potassium selenocyanate was covered with 75 ml of water and the mixture heated on a water bath for a few minutes. The potassium diselenocyanatocobaltiate formed dissolved. To the filtered solution was added ammonium chloride. A brown crystalline precipitate formed after some time. The cold mixture was transferred to a glass filter and washed with cold water and then alcohol and ether. The yield was 70-80% of theoretical. Under a microscope, the crystals appeared as rhombic prisms, beveled at the base. The salt was soluble in water.

Air-dried material was used for analysis.

Found %: Co 10.33; 10.29; Se 27.52; N 17.04; weight loss at 105°, 9.8; 10.01
$NH_4[Co(C_4H_7O_2N_2)_2(CNSe)_2] \cdot 3H_2O$. Calculated %: Co 10.31; Se 27.64; N 17.16 H_2O 9.46

A solution of this salt gave precipitates with various cations: Co^{2+} – dark brown, almost black precipitate; finely crystalline powder under a microscope. Ni – brown crystalline precipitate; the crystals appeared as tetragonal prisms under a microscope. Cu^{2+} – dark brown crystalline precipitate. Cd – finely crystalline brown precipitate. Fe^{2+} – brown precipitate; triangular prisms under a microscope. Ca – yellow-orange crystalline precipitate; under a microscope the crystals appeared as long yellow needles. Mg – long orange prisms.

Hydrogen diselenocyanato-bis-dimethylglyoximatocobaltiate $H[Co(DH)_2(SeCN)_2]$. Potassium or ammonium diselenocyanato-bis-dimethylglyoximatocobaltiate was dissolved in a small amount of hot water, the solution filtered, and HCl added. After some time the solution began to deposit a brown-red crystalline precipitate. After cooling to room temperature, the precipitate was transferred to a glass filter and washed with water, alcohol, and ether. The yield was 70-80% of theoretical.

The diselenocyanato acid could also be obtained from $1,6\text{-}[Co(H_2O) \cdot (DH)_2OH] \cdot H_2O$ [15] and potassium selenocyanate. For this purpose the reagents were measured out accurately in a ratio of 1 : 2 and heated for 15-20 min on a water bath with a small amount of water and the product precipitated with HCl. The yield was 80% of theoretical. Hydrogen diselenocyanato-bis-dimethylglyoximatocobaltiate is difficultly soluble in water and slightly more soluble in ethanol. The crystals appeared as brown-red prisms under a microscope.

•For the preparation of dimethylglyoximates of trivalent cobalt containing a selenocyanate ion, the starting materials should not contain even traces of acids.

Found %: Co 11.60; 11.65; Se 31.30; N 16.78; 16.44

$H[Co(C_4H_7O_2N_2)_2(CNSe)_2]$. Calculated %: Co 11.79; Se 31.57; N 16.67

Selenocyanato-bis-dimethylglyoximatoaquocobalt $[Co(H_2O)(DH)_2(SeCN)] \cdot H_2O$. To a solution of ammonium diselenocyanato-bis-dimethylglyoximatocobaltiate or, more simply, to the solution obtained by reacting the hydroxo aquo compound and potassium selenocyanate in a ratio of 1 : 2 was added a few drops of concentrated ammonia or alkali. Mixing the solution immediately gave a light yellow microcrystalline precipitate, which was washed on a filter several times with water, alcohol, and ether. The yield was 90% of theoretical. The substance was difficultly soluble in water and organic solvents.

Found %: Co 13.46; 13.58; 13.42; Se 18.15; 18.20

$[Co(H_2O)(C_4H_7O_2N_2)_2(CNSe)] \cdot H_2O$. Calculated %: Co 13.70 Se 18.35

Selenocyanato-bis-dimethylglyoximatopyridinecobalt $[CoPy(DH)_2SeCN]$. A mixture of 0.85 g of the chloro aquo compound $[Co(H_2O) \cdot (DH)_2Cl]$ and 0.72 g of potassium selenocyanate was heated on a water bath with 75 ml of 50% ethanol until solution was complete. To the filtrate solution was added 0.2 ml (1 mole) of pyridine. The solution immediately deposited a yellow crystalline precipitate, which was difficultly soluble in water, alcohol, and ether. Under a microscope, the crystals appeared as long tetragonal prisms.

Found %: Co 12.46; 12.48; Se 16.55

$Co(C_5H_5N)(C_4H_7O_2N_2)_2CNSe$. Calculated %: Co 12.46; Se 16.69

Selenocyanato-bis-dimethylglyoximatoanilinecobalt $Co(C_6H_5NH_2)(DH)_2SeCN$. To an aqueous alcohol solution of potassium diselenocyanato-bis-dimethylglyoximatocobaltiate, obtained by the above procedure, was added aniline (1 mole). A finely crystalline yellow precipitate was formed and this was collected on a glass filter and washed well with water, alcohol, and ether. The yield was 70% of theoretical.

Found %: Co 11.48; 11.52; N 17.30; 17.28

$Co(C_6H_7N)(C_4H_7O_2N_2)_2CNSe$. Calculated %: Co 11.66; N 17.25

Action of pyridine on hydrogen dithiocyanato-bis-dimethylglyoximatocobaltiate. When a small amount of pyridine was added to an aqueous alcohol solution, a finely crystalline yellow precipitate of thiocyanato-bis-dimethylglyoximatopyridinecobalt was obtained in 80% of theoretical yield.

Found %: Co 13.68; S 7.40; N 19.65

$CoC_5H_5N(C_4H_7O_2N_2)_2CNS$. Calculated %: Co 13.82; S 7.50; N 19.71

Bis-dimethylglyoximato-dipyridinecobalt selenocyanatonitro-bis-dimethylglyoximatocobaltiate $[CoPy_2(DH)_2][Co(DH)_2NO_2(SeCN)]$. Solutions of 1.75 g of nitro-bis-dimethylglyoximatoaquocobalt in 50 ml of alcohol and 0.77 g of potassium selenocyanate in 20 ml of alcohol were mixed and the mixture heated for 20 min on a water bath. To the filtered solution was added 2.5 g of bis-dimethylglyoximato-dipyridinecobalt nitrate in 40 ml of water. After some time a yellow crystalline precipitate was formed and this was collected on a glass filter and washed several times with water, alcohol, and ether. The yield was 70% of theoretical.

Under a microscope the substance appeared as long yellow platelets. It was difficultly soluble in water, but slightly more soluble in alcohol.

Found %: Co 13.15; 13.04; Se 8.80; 9.00

$[Co(C_5H_5N)_2(C_4H_7O_2N_2)_2][Co(C_4H_7O_2N_2)_2CNSeNO_2]$. Calculated %: Co 13.29; Se 8.90

When an alcohol solution obtained as described above by heating nitro-bis-dimethylglyoximatoaquocobalt and potassium selenocyanate was treated with a few drops of dilute alkali or ammonia, a precipitate of selenocyanato-bis-dimethylglyoximatoaquocobalt $[CoH_2O(DH)_2SeCN] \cdot H_2O$ was formed.

Found %: C 13.62; Se 18.25

Calculated %: Co 13.70; Se 18.55

Chloro-bis-dimethylglyoximatoselenocarbamidecobalt $Co(SeCN_2H_4)(DH)_2Cl$. A mixture of 3.4 g of chloro-bis-dimethylglyoximatoaquocobalt and 1.23 g of selenourea was covered with 75 ml of water. Even when the mixture was stirred at room temperature, the gray-green chloro aquo compound changed completely to a yellow-brown substance. To complete the reaction, the precipitate was heated for 15 min on a water bath and was then collected on a glass filter and washed with water, alcohol, and ether. The yield was 80% of theoretical.

Under a microscope the substance appeared as a finely crystalline yellow powder.

Found%: Co 13.06; 12.94; 13.15; 13.10; N 18.69; 18.72

$CoCH_4N_2Se(C_4H_7O_2N_2)_2Cl$. Calculated%: Co 13.17; N 18.76

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••See C. B. translation.

EQUILIBRIUM IN THE SYSTEM $V_2C - H_2 - CH_4 - V$

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(Presented by Academician G. V.Kudryumov, March 25, 1960)
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Original article submitted March 25, 1960

Data on the free energies of formation of transition metal carbides are important for solving a number of problems in theoretical metallography. In particular, they may be used for predicting the solubility of carbides of alloying elements in solid solutions based on iron and other metals.

Transition metals in the fourth period of the Periodic Table to the left of iron have an extremely high affinity for carbon. As a result, the study of equilibria in which the carbides of such elements participate involves great difficulties. The literature contains data predominantly on the heats of formation of these carbides. In a number of cases these data are very contradictory. It should also be emphasized that as a rule, transition metal carbides are phases of variable composition [1]. Moreover, in many investigations of the thermodynamics of these carbides there is no information on the structure and composition of the equilibrium phases. For the reasons listed, reliable data on the thermodynamics of carbides of such elements as Ti, V, Cr, and Mn are limited.

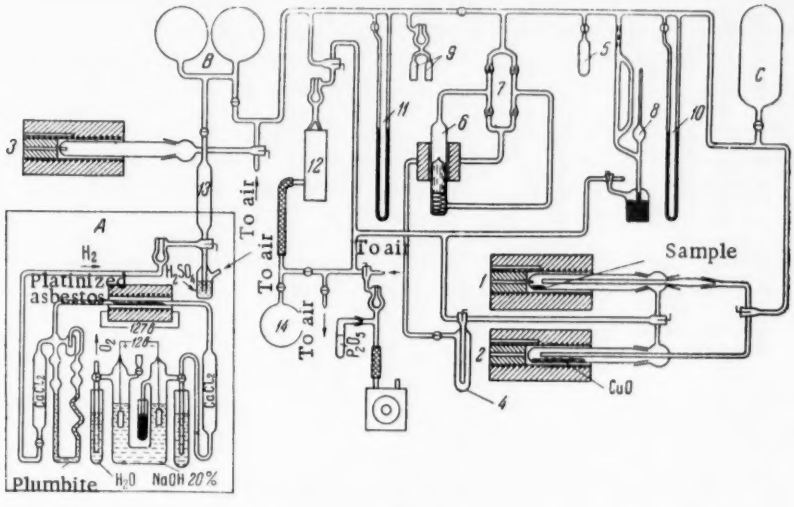

Fig. 1.

Available data on vanadium carbide are based on a measurement of the equilibrium pressure of CO over a mixture of vanadium, vanadium carbide, and vanadous oxide at one temperature (1613°K). In this case it was assumed that the carbide corresponded to the composition VC. By using data on heat capacity and this measurement,

Fig. 2.

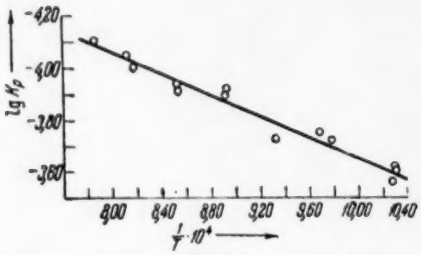

Fig. 3.

Richardson [2] found an approximate equation for the free energy of formation of VC from the elements:

$$\Delta G^0_{298-2000^\circ K} = -12500 + 1{,}6T. \qquad (1)$$

The present communication gives the results of a determination of the free energy of formation of a vanadium carbide close in composition to V_2C and in equilibrium with metallic vanadium. The structure of the carbide was checked by x-ray structural analysis. We studied the equilibrium

$$V_2C_{(s)} + 2H_{2(g)} = CH_{4(g)} + 2V_{(s)}. \qquad (2)$$

The equilibrium constant of this reaction $K_p = \frac{P_{CH_4}}{P^2_{H_2}}$ was determined by means of the apparatus illustrated in Fig. 1, which consisted of the following components: A) electrolyzer; B and C) gas-storage vessels; 3) furnace for preliminary treatment of sample in hydrogen and under vacuum; 5) calibrated vessel; 6) electromagnetic circulation pump; 7) valve device giving continuous movement of gas in one direction; 8) MacLeod gauge; 9) vacuum tubes; 10 and 11) mercury U-manometers; 12) oil diffusion pump; 13) bypass vessel; 14) forevacuum tank.

Into the quartz tube, which was contained in furnace 1 with a regulated temperature, was placed a powder of the carbide investigated and over this was circulated hydrogen and then, as reaction (2) proceeded, an H_2-CH_4 mixture. When equilibrium had been reached, the hydrogen was burned in tube 2, which contained copper oxide heated to 300°. The water vapor was frozen in trap 4 with liquid nitrogen. For kinetic reasons, the methane was not burned over the copper oxide at the given temperature [3, 4], and its pressure was measured with the MacLeod gauge. As the equilibrium of reaction (1) is strongly displaced to the left, the partial pressures of methane were very small—of the order of 10^{-3}-10^{-2} mm Hg. For this reason, in the calculation of K_p the equilibrium hydrogen pressure of the order of 190-300 mm was taken as equal to the total pressure in the circulation loop, which was measured with a mercury U-manometer (10) with a microscope to read the level.

Figure 2 gives an x-ray diffraction pattern of the sample investigated and this shows the presence of two phases, namely, metallic vanadium and a carbide with a hexagonal structure and the lattice periods a = 2.875 kX and c = 4.530 kX. According to the data in [1], this carbide corresponds to the composition V_2C. The experiments were carried out over the temperature range 700-1000°.

It was established that depending on the temperature, the equilibrium of reaction (1) was reached after 75 to 20 hr. The experimental results are given in Fig. 3 as a plot of log K_p against 1/T.

The equation of the line in Fig. 3, which was found by the method of least squares, has the form

$$\lg K_p = \frac{2201{,}9}{T} - 5{,}825 \qquad (3)$$

and for the free energy

$$\Delta G^0_{973-1273^\circ K} = -10050 + 26{,}65\ T. \qquad (4)$$

For the formation of methane according to [2]

$$C_{(s)} + 2H_{2(g)} = CH_{4(g)}; \qquad (5)$$

$$\Delta G^0_{500-2273^\circ K} = -21550 + 26{,}16\ T. \qquad (6)$$

A combination of reactions (2) and (5) and the corresponding equations for ΔG^0 gives

$$2V_{(s)} + C_{(s)} = V_2C_{(s)}: \quad (7)$$

$$\Delta G^0_{973-1273^\circ K} = -11500 - 0{,}49\ T. \quad (8)$$

Thus, over the temperature range investigated, ΔH of formation of V_2C equals -11500 ± 500 cal/mole. The change in entropy $\Delta S_{973-1273^\circ} = 0.49$ cal/mole·deg, which is within the limits of experimental error.

The value obtained for the heat of formation of vanadium carbide is somewhat less than the estimate in [2] for VC [-12500 cal/mole, according to equation (1)].

The heat of formation of a carbide with a lower carbon content should be higher. This discrepancy is apparently caused by the inaccuracy in the determination of ΔH for VC, which, as indicated above, was based on the results of one experiment at a single temperature. In addition, it cannot be certain that this carbide actually had the composition VC. Considering the value of ΔH that we found for V_2C, it can be assumed that the heat of formation of VC given in the literature [5] (-28000 cal/mole) is very high.

In steel alloyed with vanadium, the excess carbide phase is a compound which is close in composition to VC. The equation obtained in the present work for the free energy of formation of V_2C may be used for calculating the limiting concentrations of carbon in the solid solutions under conditions where the excess phase is this carbide in the same way as the solubility of carbon in α-Fe was calculated [6]. In addition, equation (7) makes it possible to carry out calculations on other equilibria involving the carbide V_2C.

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FORMATION OF CONJUGATED DIENEAMINES BY THE REACTION OF MONO- AND DIQUATERNARY SALTS OF 1,4-DIAMINES WITH AQUEOUS ALKALI

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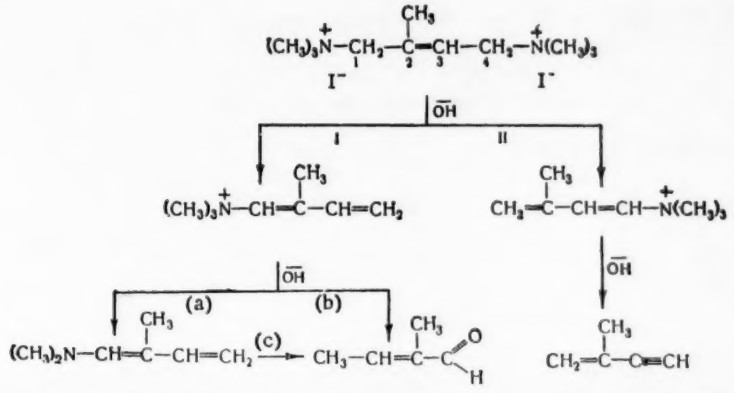
Quaternary ammonium salts containing a β,γ-unsaturated radical are readily cleaved by aqueous alkali at the 1,4 position to form compounds with conjugated multiple bonds [1-3]. Diammonium salts of similar structure undergo double 1,4 cleavage under analogous conditions [4].

The present article is devoted to the reaction of mono- and diquaternary salts of 1,4-di-(dimethylamino)-2-methylbutene-2 with aqueous alkali.

In the double cleavage of a diammonium salt it is theoretically possible that the two reactions may occur simultaneously or in succession. The dissymmetry of the common radical in the diquaternary ammonium salts we studied makes it probable that the reaction is stepwise according to one of the schemes below:

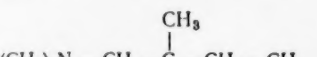


It may be considered that the induction effect of the methyl group will not produce any particular difference in the ease of protonization of the hydrogen atoms at C_1 and C_4 (vinylogy). The effect of conjugation of this methyl group should suppress protonization of the hydrogen atoms at C_4 and thus predetermine the sequence of the cleavage reactions according to scheme 1. The question of the extent to which the effect of conjugation of the methyl group determines the course of the given reaction could only be solved by experiment.

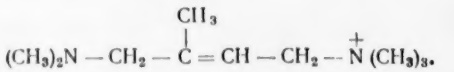
From the complex mixtures of products from the reaction of 1,4-di-(trimethylammonium)-2-methylbutene-2 iodide with aqueous alkali we were able to isolate an aldehyde, which corresponded in the analysis of its semicarbazone and molecular refraction to the dimer of methylcrotonaldehyde, and a high-boiling amine product,

which was apparently the condensation product of methylcrotonaldehyde and 1-dimethylamino-(methyl)-butadiene. The picture was repeated completely when we turned from a mixture of a quaternary ammonium salt and alkali to an ammonium base. Contrary to the statement of Slobodin [5], we were unable to detect any trace of 2-methylvinylacetylene in the reaction products and this supports scheme 1.

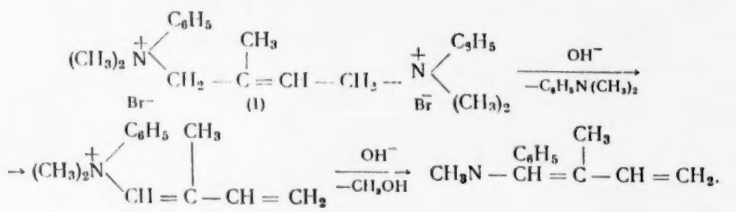
It might have been expected that the picture would be clearer in the cleavage of the monoiodomethylate of 1,4-di-(dimethylamino)-2-methylbutene-2. For this purpose we prepared the monoiodomethylate by partial iodomethylation of 1,4-di-(dimethylamino)-2-methylbutene-2. The position of the methyl group in the monoiodomethylate was established during the study of the cleavage of the latter. The reaction of the monoiodomethylate with aqueous alkali proceeded at a lower temperature (120°), but still gave the same products as in the cleavage of the diquaternary salt, differing only in better yields of these products and an appreciable decrease in the amount of tarry products. The hydroxide obtained by treatment of the monoiodomethylate of 1,4-di-(dimethylamino)-2-methylbutene-2 with an aqueous suspension of silver oxide was then cleaved in vacuum. The cleavage occurred mainly at a reaction mixture temperature of 105-107°. By this method we were able to isolate 1-dimethylamino-2-methylbutadiene-1,3 in about 40% of theoretical yield. This compound was stable and could be distilled at atmospheric pressure and stored without change. It underwent most reactions of carbonyl compounds, reacting with semicarbazide solution, with 2,4-dinitrophenylhydrazine, and with hydroxylamine to form dimethylamine and the corresponding derivative of α-methylcrotonaldehyde. It gave a silver mirror with an ammonia solution of silver oxide and a crystalline adduct with maleic anhydride. The formation of α-methylcrotonaldehyde derivatives indicates that the methyl group was in the β-position relative to the amino group in the dieneamine:



and consequently in the starting monoiodomethylate:



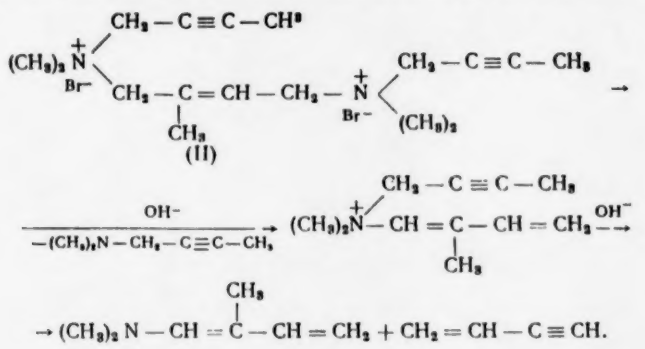
The data obtained indicate that the second stage of the cleavage of the diiodomethylate [stage (a), scheme 1] requires a higher temperature (140-145°). In this connection it was interesting to investigate the reaction of alkali with two more diquaternary ammonium salts: 1,4-di-(dimethylphenylammonium)-2-methylbutene-2 bromide (I) and 1,4-di-(dimethylbutyn-2-ylammonium)-2-methylbutene-2 bromide (II). With these compounds, stage (a) should be facilitated by the fact that the ammonium complex contains, in the first case, a phenyl radical, which facilitates the cleavage, and in the second case, the butyn-2-yl radical, which is readily eliminated. Alkaline cleavage of salt I proceeded under much milder conditions (boiling water bath temperature) and gave a mole of dimethylaniline and 1-methylphenylamino-2-methylbutadiene-1,3 (80%).



The structure of the latter was demonstrated by its conversion to methylaniline and α-methylcrotonaldehyde semicarbazone by the action of semicarbazide. In contrast to 1-dimethylamino-2-methylbutadiene-1,3, 1-methylphenylamino-2-methylbutadiene-1,3 began to change immediately after distillation and became red and formed tar after brief storage.

The cleavage of salt II proceeded analogously. The products from the cleavage of this salt in vacuum were molar amounts of 1-dimethylaminobutyne-2, vinylacetylene, 1-dimethylamino-2-methylbutadiene-1,3,

and conversion products of the latter. The reaction proceeded according to the scheme:



Thus, the alkaline cleavage of diquaternary ammonium salts I and II proceeded stepwise according to scheme I through stage (a), while stages (b) and (c) did not occur.

1,4-Di-(dimethylamino)-2-methylbutene-2 was obtained by reaction of 1,4-dibromo-2-methylbutene-2 with 60% aqueous dimethylamine solution. The yield was 41% and the product had b.p. 71-72°/10 mm, d^{20}_4 0.8095; $n^{20}D$ 1.4453; found %: N 18.23; calculated %: N 17.95; m.p. of picrate 172°.

The monoiodomethylate of 1,4-di(dimethylamino)-2-methylbutene-2 was obtained by reaction of the amine with a molar amount of methyl iodide in ether. The product dissolved readily in alcohol and water. Found % I^- 42.48; calculated 42.6. The yield of the salt was 95%. The diiodomethylate was obtained by the reaction with two moles of methyl iodide in alcohol Found % I^- 57.3; calculated 57.7.

Salts I and II were obtained by the reaction of 1,4-dibromo-2-methylbutene-2 with two moles of dimethylaniline and dimethylaminobutyne-2, respectively, in alcohol with subsequent evaporation of the alcohol at room temperature.

The salts were cleaved with aqueous alkali in the usual way [1, 4]. Below we given the physical constants and elementary analysis data for those of the cleavage products which are described for the first time:

1-Dimethylamino-2-methylbutadiene-1,3: b.p. 111-113°/680 mm, d^{20}_4 0.7902; $n^{20}D$ 1.4539; found %: N 13.42; calculated 12.70; m.p. of semicarbazone 225°; m.p. of oxime 43°; m.p. of 2,4-dinitrophenylhydrazone 220°.

Dimer of α-methylcrotonaldehyde: b.p. 71-72°/8 mm, d^{20}_4 1.0762; $n^{20}D$ 1.5305; m.p. of semicarbazone 194-195°; percent N found in semicarbazone 18.45; calculated 18.70.

1-Methylphenylamino-2-methylbutadiene-1,3: b.p. 160°/10 mm, d^{20}_4 0.9832; $n^{20}D$ 1.5900; found %: N 8.23; calculated %: N 8.09; gives the same derivatives as 1-dimethylamino-2-methylbutadiene-1,3.

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AZOBENZENE AS AN ACCEPTOR OF HYDRIDE HYDROGEN

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In attempting to elucidate the specifically favorable role of acetone in the preparation of onium and organometallic compounds from arenediazonium fluoborates, we investigated the behavior of benzenediazonium fluoborate in ketones and found that together with the normal decomposition with the liberation of hydrogen, in some cases in a remarkable way there was reduction of the benzenediazonium and formation of the ketone phenylhydrazone, which rearranged into the corresponding indole. We are reporting on this reaction separately. Extending the study of this unusual reduction of two bound nitrogen atoms to the case of azobenzene, we carried out the reaction of azobenzene in the presence of boron trifluoride as catalyst.

In the case of ketones such as cyclohexanone, which give indole ring closure under the action of a diazonium fluoborate, we also obtained the corresponding indole from azobenzene. Thus, cyclohexanone yielded the same tetrahydrocarbazole. Instead of the elimination of ammonia as in the normal Fischer synthesis, in our case the azobenzene lost aniline. This cycle of reactions will be elucidated separately in the very near future.

Together with this reaction, there was almost always a benzidine rearrangement of azobenzene. We replaced the boron trifluoride by concentrated sulfuric acid. It was found that not only in ketones, but in almost all organic solvents the azobenzene abstracted hydrogen from the latter and rearranged into benzidine. Thus, azobenzene reacted with ketones: acetone (at the b.p., 74.6%*), cyclohexanone (100°; 51.6%); acids: formic (b.p., 74.6%), acetic (b.p., 10.7%), succinic,** benzaldehyde (b.p., 81%), dibutyl ether (100°, 77%), benzene (b.p., 79%), thiophene (b.p., 76%), nitrobenzene (140-150°, 64%), cyclohexane (b.p., 7.5%), n-hexane (b.p., 22%), benzyl alcohol (18°, 47%), and cycloheptatriene (18°, 70%). The reactions were carried out in excess of the organic compound. In the case of formic acid, benzaldehyde, cycloheptatriene, and benzyl alcohol, the reaction products were benzidine with some diphenyline and the dehydrogenation product of the reagent, i.e., CO_2, benzoic acid, the tropylium cation, and benzaldehyde, respectively.

In the case of all the other organic solvents, which also formed benzidine with azobenzene under the given conditions, they themselves were converted to tar—a black, infusible, finely disperse powder, containing carbon (54-65%), hydrogen (3-4%), nitrogen (3-9%), sulfur (2-3% and in the case of thiophene, 21%), and an ash in the form of sodium sulfate (0.5-11%). Depending on the organic compound, the reaction time varied over a wide range from 30 min in benzaldehyde to 10 hr in benzene. The reaction also occurred if the sulfuric acid was replaced by pyrophosphoric or fluoboric acids, but as catalysts they were weaker than sulfuric acid.

It is interesting that in the reaction of azobenzene with acetone, in addition to benzidine and diphenyline, we also found phenyl isocyanide in the reaction products. A very small amount of phenyl isocyanide was also

*The reaction temperature and yield of benzidine with diphenyline, calculated on the azobenzene reacting, are given in parentheses.

**Carbon tetrachloride was used as the solvent for the reaction with succinic acid.

obtained in the reaction of azobenzene with boiling acetic acid. Engler and Schestopal [1] mentioned that considerable amounts of benzidine are formed when azobenzene is boiled with zinc chloride and acetone.

The optimal amount of sulfuric acid was established in the reaction with formic acid from the amount of carbon dioxide liberated (determined as $BaCO_3$). The molar ratio of azobenzene and sulfuric acid equaled 1 : 2. A mixture of azobenzene and sulfuric acid in this ratio formed a dry, yellow powder.•

The remarkable capacity of azobenzene to abstract hydrogen from such stable compounds as benzene, nitrobenzene, cyclohexane, and n-hexane, and also the absence of a reaction with chloroform and nitromethane, which have a labile (readily protonized) hydrogen, gave us grounds for proposing the following mechanism for the reduction of azobenzene: The electrophilic reagent (H_2SO_4, H_3PO_4, HBF_4, $ZnCl_2$, HCl, HBr) gives a salt with azobenzene•• $[C_6H_5-N=N-C_6H_5]^+HSO^-$. The cation formed abstracts a hydrogen with a pair of electrons (hydride hydrogen) from the organic compound, forming hydrazobenzene, which, in its turn, rearranges to benzidine.

$$[C_6H_5-N=N-C_6H_5]^+HSO_4^- + H{:}C\!\!\!\diagup\!\!\!\diagdown \rightarrow C_6H_5NH-NH-C_6H_5 + C^{+}\!\!\!\diagup\!\!\!\diagdown + HSO_4^-.$$

In most cases, the carbonium cation formed from the organic donor of the hydride anion is evidently stabilized by the elimination of a proton and the formation of a multiple bond. The unsaturated compound formed polymerizes readily in the presence of sulfuric acid. The reaction mechanism we propose is substantiated by the particular ease of the reaction at room temperature between azobenzene and tropylidene and benzyl alcohol, which readily donate hydride hydrogen [3]. The tropylidene forms a tropylium salt and benzyl alcohol forms benzaldehyde.

The formation of benzoic acid and carbon dioxide by the reaction of azobenzene with benzaldehyde and formic acid also indicates the reduction of azobenzene by hydride hydrogen as both benzoic acid and carbon dioxide may be obtained only as a result of the elimination of hydride hydrogen [4].

The conversion of azobenzene to benzidine in inorganic acids (HCl and dilute H_2SO_4) was first observed by N. N. Zinin [5] and later Verigo [6] showed that the reaction occurs when azobenzene is boiled with hydrobromic acid. Tikhvinskii [7] and then Jacobson [8] studied the mechanism of the reaction discovered by N. N. Zinin. Tikhvinskii carried out the reaction in glacial acetic acid at 100°, passing in a stream of dry hydrogen chloride or hydrogen bromide, and Jacobson studied the reaction in methanol saturated with hydrogen chloride.

In both cases the authors reported the formation of mono- and dihaloanilines together with benzidine. We decided to check whether the reaction of azobenzene with boiling hydrohalic acids proceeds differently to the reactions with organic donors of a hydride anion just described.

Azobenzene reacted completely when boiled in 40% hydrobromic acid for 3 hr. From the reaction products we isolated benzidine and bromobenzidine and it was shown chromatographically that the latter contained dibromobenzidine. When azobenzene was boiled in concentrated hydrochloric acid, part of it (49%) reacted and formed benzidine, chlorobenzidine, and dichlorobenzidine. Neither with hydrochloric acid nor with hydrobromic acid did we detect mono- or dihaloanilines, even though we used the method described by Tikhvinskii; their absence was demonstrated by paper chromatography [9].

It is evident that the azobenzene salt abstracts a hydride anion even from aqueous solutions of hydrogen halides, as from organic substances, while the remaining positive halogen ion halogenates benzidine. Thus, salts of azobenzene with strong acids are the strongest acceptors of hydride hydrogen, stronger than carbonium cations. The abstraction of a hydride anion from benzene, thiophene, and other aromatic compounds is particularly interesting. It is possible that Wittig's dehydrobenzene and its analogs are formed and these polymerize to a tar in the presence of sulfuric acid. We are studying this aspect of the problem at the present time.

•The azobenzene was recovered after this mixture had been heated for 3 hr on a boiling water bath.

••Analogous salts of azobenzene with perchloric acid were isolated and studied by Jaffé [2].

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INVESTIGATION OF THE MECHANISM OF ACETYLENE HYDRATION BY THE KUCHEROV REACTION WITH THE AID OF DEUTERIUM

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Despite the wide industrial application of the Kucherov reaction and the voluminous literature on it [1-3], the mechanism of this process is still far from clear. In particular, until recently there have been disputes and experimental studies on the stage determining the hydration rate and the participation of water or acid molecules in the transition complex of the slow stage [2, 3]. Likewise, there is no single opinion on the composition and structure of the intermediate mercury compounds of acetylene whose hydrolysis leads to the formation of acetaldehyde [1].

In developing a method of synthesizing deuteroacetaldehydes by the Kucherov reaction, we hydrated normal acetylene with D_2O solutions and deuteroacetylene with normal water. The results of these experiments shed light on the unexplained aspects of the mechanism of acetylene hydration mentioned above.

EXPERIMENTAL

We hydrated acetylene with solutions with the following composition: H_2O or D_2O 25 ml, $HgSO_4$ 4.7 g, $Fe_2(SO_4)_3$ 3.8 g, and H_2SO_4 (d = 1.84) 10.6 g. The hydration solution was placed in a glass column (l = 660 mm, d = 12 mm) packed with broken glass. Acetylene from a gasometer was passed through the column at 75-80°; the optimal rate was 10-12 liters of acetylene per hour. Under these conditions the vapor of the acetaldehyde formed was carried along by the unreacted acetylene. The gaseous products from the column were passed through a reflux condenser and a calcium chloride tube to remove moisture and were then condensed in two successive traps at -80 and -190°. Acetaldehyde with a small amount of dissolved acetylene collected in the first trap, while the second trap collected almost pure acetylene, which was then returned for hydration.

The acetaldehyde was purified by distillation, with the vapor of the distillate passed through calcium chloride and condensed at 0°. Two distillations were sufficient to yield a product which began to boil at 20.5° and distilled without residue over a range of one degree. The acetaldehyde yield was 40% on the acetylene consumed.

As we were interested not only in the total deuterium content of the acetaldehyde molecules formed, but also in its distribution between the methyl and aldehyde groups, we oxidized a sample of the aldehyde obtained to acetic acid. For this purpose, a 30% aqueous solution of acetaldehyde, cooled to 0°, was added dropwise under the surface of a solution of potassium permanganate in 20% aqueous sulfuric acid at 60-70° with continuous stirring. The drops of aldehyde reacted instantaneously on entering the oxidant solution, making it possible to reduce to a minimum the exchange between the aldehyde oxidized and the medium. Control experiments on the oxidation of normal acetaldehyde in an oxidant prepared with D_2O showed that under the conditions given the isotopic exchange with the medium was insignificant, as in three parallel experiments the potassium acetate obtained contained less than 1% of the deuterium of the oxidant solution.

TABLE 1

Deuterium Content in γ

Expt. No.	In hydration solution		In water from combustion			
	before expt.	after expt.	CH_3CHO	CH_3COOK found	CH_3COOK calc.	unreacted $CH \equiv CH$
1	27 860	—	9150	11 560	12 200	—
2	—	—	3520	4 860	4680	—
3	—	—	1550	2 040	2060	—
4	11 900	12 400	4000	—	5300	—
5	11 900	12 800	3900	—	5200	9
6	11 900	12 400	3900	—	5200	12

TABLE 2

Hydration of Labeled Acetylene in H_2O (deuterium content in γ)

Expt. No.	In $CH \equiv CH$	In water from combustion				Found calc.	In CHO group
		CH_3CHO found	CH_3CHO calc.	CH_3COOK found	CH_3COOK calc.		
1	12 800	4200	5700	1800	3800	0,48	11 400
2	6 400	2200	2840	1040	1900	0,55	5680
3	6 400	2200	2990	960	1980	0,49	5980
4	11 800	4200	5600	1860	3700	0,50	11 200
5	22 100	8600	11 200	4000	7500	0,53	22 400

The results of experiments on the hydration of normal acetylene with solutions containing D_2O are presented in Table 1.

Comparison of the data on the isotopic composition of the acetaldehyde and the potassium acetate obtained from it (Table 1) shows that in the synthesis of acetaldehyde from $CH \equiv CH$ and D_2O, the whole of the deuterium in the acetaldehyde was concentrated in the methyl group. This follows from the fact that the removal of hydrogen of the carbonyl group by oxidation increased the deuterium content of the acetate in comparison with the starting aldehyde in a ratio of 4 : 3, as follows from calculation. The absence of deuterium from the carbonyl group of acetaldehyde is in accord with its absence from acetylene isolated from the reaction medium and shows that the isotopic composition of the hydrogen of the aldehyde group was the same as the hydrogen of the starting acetylene.

If the hydration process had not been accompanied by an isotope effect or exchange with the medium, then according to the equation $CH \equiv CH + D_2O \rightarrow CHD_2CHO$, water from combustion of the aldehyde would have been twice as light as water distilled from the hydration solution. In actual fact, the deuterium in the acetaldehyde was diluted not twofold, but approximately threefold (see Table 1). Considering that in this case isotopic exchange can only enrich the aldehyde molecule in deuterium, the data obtained indicate a considerable isotope effect. The results of experiments on the hydration of acetylene labeled with deuterium by normal water are given in Table 2. It is evident that in contrast to experiments of the first series, the isotope effect is excluded from these experiments as normal hydrogen is transferred to the acetylene molecules during the hydration. On the other hand, the effect of exchange could be detected directly by comparing the isotopic composition of the starting acetylene, the acetaldehyde, and the potassium acetate.

Table 2 gives the deuterium content of the water used for preparing the acetylene from calcium carbide. The deuterium content of the acetylene must have been the same, as the reaction of calcium carbide with water

proceeds quantitatively and we used the stoichiometric amount of water. On the basis of the results of the first series of experiments, the aldehyde obtained from labeled acetylene should have contained deuterium in the methyl and aldehyde groups. We found the deuterium content of the aldehyde group by difference, by determining the isotopic composition of the water from combustion of the acetaldehyde and the potassium acetate obtained by its oxidation, using the equation $X = 4A - 3B$, where A and B are the excess densities of the water from combustion of acetaldehyde and potassium acetate, respectively (Table 2).

An examination of the values given in Table 2 shows that the aldehyde group of the acetaldehyde contained the same amount of deuterium as the starting acetylene, in accordance with the results of the first series of experiments. The slight loss in deuterium is apparently explained by the fact that we prepared the acetylene from technical calcium carbide, which always contains hydroxide. This is confirmed by the result of the last experiment, in which the starting acetylene was burned and analyzed.

Examination of the data in Table 2 also shows that the hydration was accompanied by considerable exchange. In actual fact, had there been no exchange, the acetaldehyde would have contained a half and the potassium acetate a third of the deuterium in the aldehyde group (see columns 3 and 5). As Table 2 shows, the ratio of the experimental values to those calculated, on the assumption that exchange was absent for CH_3COOK, was quite reproducible and indicated that the hydrogen of acetylene which was incorporated into the methyl group of the aldehyde was half replaced by hydrogen from the medium during the hydration.

By determining the degree of exchange during hydration, it is possible to use the results of the first series of experiments to estimate the magnitude of the kinetic isotope effect during the transfer of hydrogen from water (or acid) to acetylene molecules on the basis of the following considerations. Had the addition of both hydrogen atoms occurred without an isotope effect, then with a hydration solution in water with an excess density of 28,000 γ, in the water from combustion of the acetaldehyde, allowing for exchange, there would have been $(28{,}000 \cdot 2 + 28{,}000 \cdot 0.5) : 4 = 17{,}500$; with a hydration solution containing 12,000 γ of deuterium, in the water from combustion of the acetaldehyde there would have been $(12{,}000 \cdot 2 + 12{,}000 \cdot 0.5) : 4 = 7500\ \gamma$, i.e., 1.8-1.9 times more than found experimentally.

In the formation of acetaldehyde, two hydrogen atoms are added to acetylene. According to existing ideas they are added in two different stages, of which only one may determine the rate of the process. In other words, transfer of only one hydrogen atom may be accompanied by an isotope effect. The decrease in the deuterium content of the water from combustion of the acetaldehyde (which contains 4 hydrogen atoms in the molecule) by a factor of 1.8-1.9 corresponds to an isotope effect of the order of $1.9 \times 4 = 7.6$, calculated on one hydrogen atom.

The presence of the isotope effect demonstrates unequivocally that the hydration rate is determined by the transfer of one of the hydrogen atoms from water (or acid) molecules to acetylene molecules and that consequently water (or acid) molecules are present in the transition complex of the slow stage. This conclusion contradicts that of Flid, Moiseev, and Kalmykova [2], who investigated the kinetics of liquid-phase hydration of acetylene and found that the effect of the oxidation potential of the medium considerably exceeded that of the pH on the reaction rate. On this basis the authors came to the conclusion that the slow stage of the process is the activation of acetylene, which is not connected with the addition of protons. To reconcile the presence of the kinetic isotope effect with the results of these authors, it is apparently necessary to assume that in the rate-determining stage there is the addition of water molecules to acetylene molecules, activated by the formation of a complex with the catalyst

$$CH \equiv CH + HgX_2 \xrightarrow{\text{fast}} CH \equiv CH \cdot HgX_2,$$

$$CH \equiv CH \cdot HgX_2 + HOH \xrightarrow{\text{slow}} CH_2 = CHOH \cdot HgX_2,$$

$$CH_2 = CHOH \cdot HgX_2 + H_3O^+ \xrightarrow{\text{fast}} CH_2 = CHOH \cdot H_3O^+ + HgX_2,$$

$$CH_2 = CHOH \cdot H_3O^+ \overset{\text{fast}}{\rightleftharpoons} CH_2 = CHOH_2^+ + H_2O,$$

$$CH_2 = CHOH_2^+ \rightarrow CH_3CHO + H^+.$$

In the formation of acetaldehyde, two hydrogen atoms are added to acetylene. According to existing ideas they are added in two different stages, of which only one may determine the rate of the process. In other words, transfer of only one hydrogen atom may be accompanied by an isotope effect. The decrease in the deuterium content of the water from combustion of the acetaldehyde (which contains 4 hydrogen atoms in the molecule) by a factor of 1.8-1.9 corresponds to an isotope effect of the order of $1.9 \cdot 4 = 7.6$, calculated on one hydrogen atom.

Our data unequivocally refute the isomerization of acetylene to isoacetylene as one of the stages in the Kucherov reaction [1],

$$CH \equiv CH \rightarrow CH_2 = C\langle,$$

$$CH_2 = C\langle + HOH \rightarrow CH_2 = CHOH,$$

as in this case hydrogen from the medium should be incorporated into the aldehyde group of the acetaldehyde and this was not observed. On the same basis we should reject mercabides, i.e., completely substituted organomercury derivatives of acetylene, for example, of type (A) [4]

$$(A)\ (XHg)_2C-CX_2,$$
$$\quad\quad\quad

PREPARATION AND PROPERTIES OF SCANDIUM DIBORIDE

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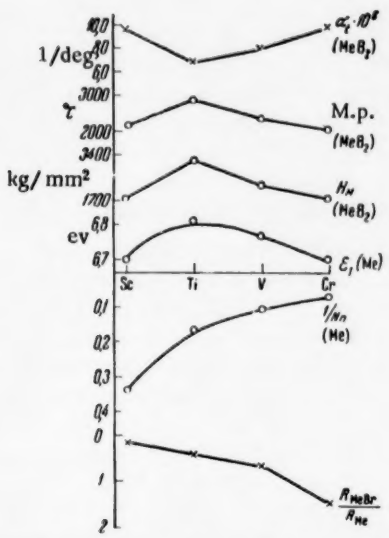
In recent years much work has been devoted to a detailed study of compounds of transition metals of the first period (titanium, vanadium, chromium, manganese, etc.) with boron, which are hard refractory compounds that are finding increasing use in various branches of technology [1]. There have been no investigations of boron compounds of the first element of the first transition period, namely, scandium, an atom of which has a $3s^23p^63d^14s^2$ electron configuration and hence the most incomplete 3d shell, with one electron.



Physical properties of Sc, Ti, V, Cr, and their diborides. $\alpha_t \cdot 10^6$ (MeB_2)—thermal expansion coefficient of diborides, 1/deg; M.p. (MeB_2)—melting point of diborides, °C; H_M (MeB_2)—microhardness of diborides (30-g load), kg/mm²; ϵ_1 (Me)—first ionization potentials of metals atoms, ev; 1/Nn (Me)—d-shell incompleteness factor of the metal atom; $\frac{R_{MeB_2}}{R_{Me}}$ is the ratio of the specific resistances of the diborides and the corresponding metal.

Therefore, it is interesting to compare the physical properties of scandium compounds with those of compounds of other transition metals of the first period, in particular, the physical properties of compounds with boron.

We have previously prepared individual samples of scandium diboride ScB_2, but they were strongly contaminated with boron carbide, from which they were separated in heavy liquids by means of the specific gravity. With preparations obtained in this way, N. N. Zhuravlev and A. A. Stepanova [2] determined the crystal structure of ScB_2 and found it to be hexagonal (AlB_2 structural type) and identical to the structures of diborides of other transition metals of Groups IV-VI, including titanium, vanadium, and chromium. The data of this work gave the following lattice periods for ScB_2: a = 3.140 ± 0.002; c = 3.510 ± ± 0.002 kX, c/a = 1.118, and density calculated from these values δ_X = 3.67 g/cc. In subsequent work, which was carried out by the author with B. M. Tsarev, G. A. Kudintseva, and V. S. Neshpor, an attempt was made to determine the basic parameters of thermionic emission of scandium diboride, but by means of x-ray analysis data it was established that when ScB_2 is heated in vacuum it loses part of the metal and changes into scandium hexaboride with a cubic lattice of the CaB_6 type with a period a = 4.355 kX. The work function of this compound was found to equal 2.96 ev and the constant A in the Richardson equation was 4.6 a/cm² · deg²; the secondary emission coefficient was 0.58 and the radiation coefficient at 1600° was 0.6.

Property	Boride phase			
	ScB_2	TiB_2	VB_2	CrB_2
M.p., °C	2250	2980	2400	2200
Microhardness, kg/mm²	1780	3370	2400	1800
Thermal expansion coeff. × 10^6	9,48	6,8	~8,0	9,8
Specific electrical resistance, μohm · cm	7—15	25,9	16,0	32,2
$R_{MeB_2} : R_{Me}$	(0,13)	0,47	0,62	1,5
First ionization potential, ev	6,7 (Sc)	6,81 (Ti)	6,74 (V)	6,7 (Cr)
d-Electron shell incompleteness factor (1/Nn)	0,333 (Sc)	0,167 (Ti)	0,111 (V)	0,067 (Cr)

In the present work we describe a systematic investigation of conditions for the preparation of scandium diboride by the reaction between Sc_2O_3 and boron in vacuum with evolution of the volatile lowest oxide of boron with the composition BO or B_2O_2: $Sc_2O_3 + 7B = 2ScB_2 + 3BO$.

It was established that maximum reaction was attained at 1800-1850° with the mixture kept at this temperature for 1 hr; the product thus obtained contained 32.6% of boron as compared with 32.5% of boron, calculated for ScB_2. The pycnometric density of the diboride powder equaled 3.65 g/cc, which agrees well with the x-ray value.

For determination of the physical properties of ScB_2, we sintered samples from the powder by hot pressing in graphite molds without a special protective atmosphere at 2000-2050° for 7-10 min with a pressure of 100 kg/cm² on the sintered powder. The microhardness of sintered ScB_2, measured with a load of 50 g, was 1742 ± 337 kg/mm², the mean density of hot-pressed samples was 3.56 g/cc, the specific electrical resistance was 7-15 μohm · cm, the temperature coefficient of the thermal emf was 7.7 μv/deg, the thermal expansion coefficient at 20-800° equaled $9.48 \cdot 10^{-6}$, and the radiation coefficient, measured over the range of 1035-1770° by the procedure in [3] was found to be practically constant and equal to 0.89 (at λ = 650 mμ). Finally, the melting point of ScB_2, determined by the procedure described in [4], equaled 2250°. The table gives a comparison of some physical properties of scandium, titanium, vanadium, and chromium diborides.

These data show that the properties which characterize the strength of the crystal lattice to some extent pass through extrema for titanium diboride with a corresponding fall in strength on the scandium diboride side and also on the side of vanadium and chromium diborides. As in the structures of diborides the boron atoms are connected to each other by covalent bonds in planar lattices in which each boron atom has three neighbors; the bond between the atoms of the boron complex and the metal atoms is largely due to the latter, which is indicated by the clear correlation between the change in melting point, microhardness, and thermal expansion coefficient of diborides on the one hand, and the primary ionization potentials of the transition metal atoms on the other. At the same time, this observation shows that these properties are mainly determined by the state of the 4s electrons, while the d electrons of the metal atoms participate much less in the bond with the boron complexes, as is shown by the lack of correlation between the change in these properties and the change in the d-electron shell incompleteness factor of the transition metals. On the other hand, the latter determines the degree of scattering of the conductivity electrons as is shown by the correlation between the values of 1/Nn, where n is the number of electrons in the d shell and N is the main quantum number of this shell [5], and the values showing the increase in the electrical resistance with the formation of borides relative to the metal. The specific electrical resistance of scandium is unknown, but by extrapolating the ratio $R_{MeB_2} : R_{Me}$ in relation to 1/Nn to ScB_2 we obtain $R_{ScB_2} : R_{Sc} = 0.13$ and hence the resistance of scandium should lie within the range of 55 to 115 μohm · cm. Thus, the relation between the resistance of diborides and the scattering capacity of the d shells confirms the previous ideas on this problem expressed in [6].*

*By using the data from this work it may be assumed that the specific electrical resistance of scandium equals ~ 90 μohm · cm and hence the most probable value for the specific electrical resistance of ScB_2 is 11.7 μohm · · cm.

Consequently, scandium diboride is a compound whose properties are such that it can be arranged in the series $ScB_2-TiB_2-VB_2-CrB_2$ and considered as the end member of this series with the strength of the ScB_2 crystal lattice determined predominantly by the state of the s electrons and the electrical properties by the state of the d electrons, as also applies to diborides of other metals of the first transition period.

In conclusion we should note the unusual similarity of the melting points, hardnesses, and thermal expansion coefficients of ScB_2 and CrB_2, which with the high electrical conductivity and hence thermal conductivity of ScB_2 and also its specific gravity, which is 35% less than that of CrB_2, offers promise of the use of ScB_2 in light refractory alloys where chromium boride is used at the present time [7].

O. I. Shulishova helped with the experimental work.

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PREPARATION OF TITANYL OXALATES OF DIVALENT METALS AND A PHYSICOCHEMICAL STUDY OF THEIR THERMAL DECOMPOSITION

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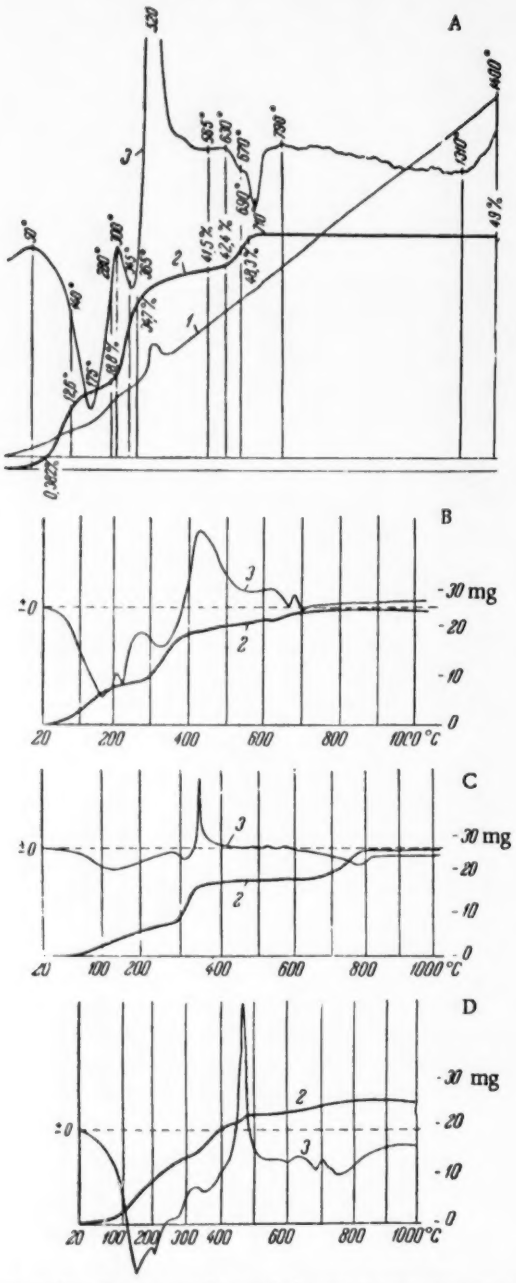
Titanium in the form of the titanyl ion is known to be capable of forming complex compounds with the oxalate ion. Thus, titanyl hydrogen oxalate with the composition $H_2[TiO(C_2O_4)_2] \cdot 2H_2O$ and some salts of this acid have been obtained in the solid state, but the only salt with a divalent cation that could isolated was the barium salt [1, 2].

The present work was devoted to the synthesis of salts of titanyl hydrogen oxalate with divalent cations and a physicochemical study of the thermal decomposition of these salts. We developed a procedure which made it possible to prepare both barium titanyl oxalate and also strontium, lead, and calcium titanyl oxalates. The procedure was as follows. A concentrated solution of oxalic acid was added with stirring to an aqueous solution of titanium tetrachloride (0.2-0.3 g/ml), prepared by the method in [3]. To the solution of titanyl oxalate obtained was added an aqueous solution of an appropriate salt of a divalent cation (barium chloride, strontium chloride, or lead nitrate) at room temperature with continuous stirring. The complex salts formed separated as white precipitates. Barium, strontium, and lead titanyl oxalates were prepared by this method. As we were unable to obtain calcium titanyl oxalate in aqueous solution under these conditions, this complex salt was synthesized in an acetone medium. An acetone solution of titanium tetrachloride was prepared analogously to the aqueous solution. The precipitate formed was washed carefully with acetone. A white powder of calcium titanyl oxalate was obtained as a result. Chemical analyses of the compounds obtained for divalent metal oxides, titanium dioxide, oxalate ion, and water are given below.

$BaTiO(C_2O_4)_2 \cdot 4H_2O$.	Found %	MeO 33,72; 33,83 TiO_2 17,57; 17,62; $C_2O_4^{''}$ 38,72; 38,84; H_2O 17,03; 16,67
	Calculated %:	MeO 34,13; TiO_2 17,78; $C_2O_4^{''}$ 39,19 H_2O 16,03
$SrTiO(C_2O_4)_2 \cdot 5,5H_2O$.	Found %:	MeO 24,28; 24,36; TiO_2 18,72; 18,78; $C_2O_4^{''}$ 41,25 41,38; H_2O 23,25; 23,24
	Calculated %:	MeO 24,29; TiO_2 19,73; C_2O_4 41,26; H_2O 23,22
$PbTiO(C_2O_4)_3 \cdot 4H_2O$.	Found %:	MeO 36,67; 36,82; TiO_2 13,13; 13,18; $C_2O_4^{''}$ 43,38 43,56; H_2O 12,07; 11,72
	Calculated %:	MeO 36,76; TiO_2 13,16; $C_2O_4^{''}$ 43,89 H_2O 11,87
$CaTiO(C_2O_4)_2 \cdot 5H_2O$.	Found %:	MeO 15,12; 15,20; TiO_2 21,54; 21,65; $C_2O_4^{''}$ 47,46 47,70; H_2O 24,50; 24,11
	Calculated %:	MeO 15,15; TiO_2 21,59; $C_2O_4^{''}$ 47,56; H_2O 24,34



Complex thermographic and thermogravimetric investigation of the thermal decomposition of the following titanyl oxalates: A) Barium; B) strontium; C) lead; D) calcium; 1) simple thermocouple; 2) thermogravimetric; 3) differential thermocouple.

Analysis showed that the compounds obtained had the compositions: $BaTiO(C_2O_4)_2 \cdot 4H_2O$; $SrTiO(C_2O_4)_2 \cdot 5.5H_2O$; $PbTiO(C_2O_4)_3 \cdot 4H_2O$; and $CdTiO(C_2O_4)_2 \cdot 5H_2O$.

X-ray phase analysis data and the results of crystallooptical investigations showed that the complex salts obtained formed fine isotropic crystals. The refractive indices, determined by the immersion method, were as follows: $N = 1.66_6$ for barium titanyl oxalate, $N = 1.62_1$ for strontium titanyl oxalate, $N = 1.59_3$ for calcium titanyl oxalate, and $N > 1.78$ for lead titanyl oxalate.

Complex thermographic and thermogravimetric investigation showed that the thermal decomposition of barium, strontium, lead, and calcium titanyl oxalates has a stepwise character and is accompanied by a series of endothermal and exothermal processes (figure). As the data of x-ray phase, thermogravimetric, and chemical analyses showed, at first the water of crystallization was liberated when the compounds were heated and the salts changed to an amorphous state. For barium and lead titanyl oxalates, this process was accompanied by one endothermal effect at 175 and 140°, respectively; for strontium titanyl oxalate there were two (170 and 230°), and for calcium titanyl oxalate there were three endothermal effects (160, 220, and 260°). (The liberation of water of crystallization was reversible and the dehydrated salts were capable of adding all the water lost during heating.) Then, at almost the same temperature (320-360°), all the salts examined showed an endothermal effect, which was connected with decomposition of the oxalate groups and the liberation of carbon dioxide. This indicates that the oxalate groups apparently are mainly attached to the titanyl ion and the cation has no appreciable effect on the strength of this bond. With the exception of the case of calcium titanyl oxalate, the exothermal process occurring after decomposition of the oxalate groups was not accompanied by a sharp loss in weight. As x-ray phase analysis showed, this process was connected with the formation of barium, strontium, lead, and calcium metatitanates. Further heating led to complete removal of the carbon monoxide remaining in the salts and this was accompanied by a sharp loss in weight and endothermal effects. Thus, the thermal decomposition of barium, strontium, lead, and calcium titanyl oxalates was complete by approximately 800° for all the salts. Reheating of the final decomposition products of the salts was accompanied by hardly any thermal effects, indicating the irreversibility of the complete thermal decomposition of the divalent metal titanyl oxalates obtained.

From the data of chemical and x-ray phase analysis it follows that the final decomposition products of barium, strontium, lead and calcium titanyl oxalates were the metatitanates of these metals with a structure of

Firing temperature, °C	Specific gravity, g/cc			
	$BaTiO(C_2O_4)_2 \cdot 4H_2O$	$SrTiO(C_2O_4)_2 \cdot 5.5H_2O$	$PbTiO(C_2O_4)_2 \cdot 4H_2O$	$CaTiO(C_2O_4)_2 \cdot 5H_2O$
Room	$2,27_9$	$2,11_8$	$2,84_1$	$1,45_9$
230	$3,10_7$	$2,58_5$	$3,83_4$	$2,44_2$
300	—	—	—	—
370	$3,67_2$	$3,18_2$	5,74	$2,77_5$
600	$5,05_8$	$4,46_8$	$6,57_9$	$3,45_4$
850	5,98	$4,76_7$	7,52	$4,09_9$

the perovskite type. In parallel we determined the specific gravities of the starting salts and their thermal decomposition products (see the table). As was to be expected, the specific gravity of the salts increased with a rise in the firing temperature and the removal of the volatile decomposition products to a maximum value, corresponding to the specific gravities of barium, strontium, calcium, and lead titanates.

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DEHYDROGENATION OF BUTANE – BUTYLENE MIXTURES ON AN ALUMINUM – CHROMIUM CATALYST•

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In previous work [1] an investigation was made of the dehydrogenation of butane–butylene mixtures on two catalysts samples: an aluminum–chromium catalyst and a mixed oxide catalyst for the dehydrogenation of butylene. Dilution with water vapor was used in experiments with the mixed oxide catalyst but no diluent was used with the aluminum–chromium catalyst as water vapor was found to retard the dehydrogenation of butane to butylene and promote cracking of these hydrocarbons with the formation of decomposition products and carbon on the catalyst. In the dehydrogenation of butane–butylene mixtures on the aluminum–chromium catalyst at atmospheric pressure with a short contact time, the butadiene yields were lower than on the oxide catalyst. Thus, at 600-635°, the butadiene yields were 10-11.6% on the mixture passed and 44-49.5% on the reacted mixture; with an oxide catalyst and dilution with water vapor, butadiene was obtained in a yield of 19.8% on the butane–butylene mixture passed and 75-80% on that reacted.

The present work was designed to obtain data on the kinetics and mechanism of the dehydrogenation of butane–butylene mixtures on an aluminum–chromium catalyst. Under the optimal conditions for the investigation, we measured the dehydrogenation rates of butane and binary mixtures of the starting material and reaction products: butane–butylene, butane–butadiene, and butane–hydrogen. As butylene and butadiene were decomposed on the catalyst, to determine the degree of decomposition we measured the reaction rates in binary mixtures of these hydrocarbons with ethane, considering that ethane occupies the same part of the active surface as butane, but is not dehydrogenated or decomposed.

EXPERIMENTAL

The experiments were carried out by a flow method in a quartz tube 16 mm in diameter, with 4 ml of catalyst [2]. To avoid the presence of moisture, the hydrocarbons, which were introduced from a gasometer, were dried by passage through a column with $CaCl_2$. The catalyzate gas was collected in a gasometer over a saturated solution of sodium chloride. The gases were analyzed on a Podbelniak apparatus and on Bushmarin and modified Orsat–Yeger apparatuses. The gas volumes were corrected to n.t.p. Experiments with butane and mixtures of it with butylene, butadiene, and hydrogen were carried out over the temperature range 600-635° with a flow rate of 1200 liter/liter/hr.

The dehydrogenation of butane at 600° formed about 47% of butylene and 5.4% of butadiene on the butane passed. With an increase in temperature, the degree of decomposition of the hydrocarbons increased and the butylene yields fell to 38.0% at 620° and 32.2% at 635°. The amount of butadiene formed remained unchanged (Table 1).

•Work carried out in 1950; the aluminum–chromium catalyst was presented by M. N. Markushkin [6].

TABLE 1

Dehydrogenation of Butane and Butane–Hydrogen Mixtures. Flow Rate v = 1200 liter per liter/hr

Temp., °C	Substance passed	Analysis, vol. %						Obtained, %	
		C_2H_4	C_3H_6	C_4H_8	C_4H_6	H_2	C_nH_{2n+2}	C_4H_8	C_4H_6
600	C_4H_{10}	1,0	1,5	2,7	23,5	36,0	35,3	46,8	5,4
620	The same	2,2	2,1	2,6	19,0	36,9	36,4	38,0	5,2
635	The same	3,8	2,8	2,8	15,6	34,4	40,0	32,2	5,6
600	C_4H_{10} 78,2% + + H_2 21,8%	1,0	1,3	2,4	20,4	74,9		36,0	4,2
620	The same	2,0	2,0	2,4	16,4	7,27		29,7	4,3

TABLE 2

Dehydrogenation of Butane–Butylene Mixtures, v = 1200 liter/liter/hr

Temp., °C	Mixture compn., mole %		Analysis, vol. %				Degree of decomposition of C_4H_8, %	C_4H_6 obtained on mixture passed, %
	C_4H_{10}	C_4H_8	C_2H_4	C_3H_6	C_4H_6	C_4H_8		
600	51,8	48,2	1,7	3,1	4,8	20,4	14,0	8,0
620	51,8	48,2	3,0	4,3	4,6	17,4	17,3	8,2
635	51,8	48,2	3,7	6,0	4,0	13,7	22,2	7,6

TABLE 3

Dehydrogenation of Butylene-Ethane and Butadiene–Ethane Mixtures, v = 1200 liter per liter/hr

Temp., °C	Composition of mixture, mole %	Analysis, vol. %						Degree of decomposition, %	Formed, %	
		C_2H_4	C_3H_6	C_4H_8	C_4H_6	H_2	C_nH_{2n+2}		C_4H_6	carbon
600	C_4H_8 50,4% + + C_2H_6 49,6%	3,6	2,0	2,4	16,8	29,6	45,6	50,1	7,2	20,0
620		4,2	2,8	2,4	14,6	31,7	44,3	54,5	7,4	21,4
635		5,2	3,2	2,0	12,2	29,4	48,0	59,0	6,7	28,9
600	C_4H_6 18,0% + + C_2H_6 82,0%	2,2	3,3	0,8	—	22,0	71,7	96,0	—	42,0
620		3,2	3,9	0,3	—	25,2	67,1	98,0	—	44,0
635		3,3	4,1	—	—	30,2	62,4	100,0	—	46,0

Mixtures of butane and hydrogen. The experiments were carried out at 600 and 620° under the same conditions as with pure butane. The mixtures contained 21.8 mol.percent of hydrogen. These experiments showed that the amount of butylene formed on the mixture passed fell by 1% in comparison with the dehydrogenation of pure butane. In all probability this is explained by the occurrence of the reverse reaction, namely, hydrogenation of butylene (Table 1).

Mixtures of butane and butylene. The mixtures contained 48.2 mol. percent of butylene. The results obtained are given in Table 2. In these experiments, up to 8% of butadiene was formed and there was decomposition of butylene (from 6 to 14.6% at 600-635°) with the formation of light hydrocarbons. In order to allow for the decomposition of butylene, we carried out experiments with mixtures of butylene and ethane.

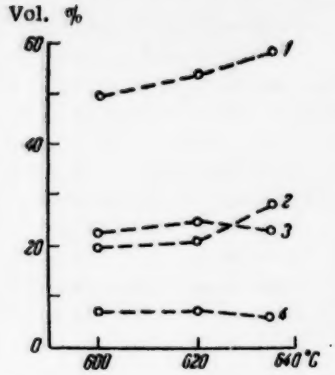

Fig. 1. Decomposition of butylene in relation to temperature: 1) C_4H_8 (decomp.); formation of: 2) carbon; 3) light hydrocarbons; 4) C_4H_6.

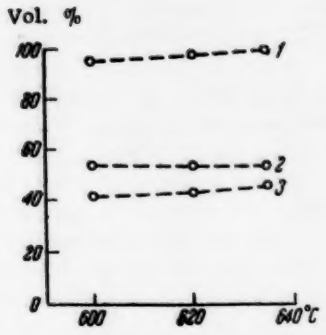

Fig. 2. Decomposition of butadiene in relation to temperature: 1) C_4H_6 (decomp.); formation of: 2) light hydrocarbons; 3) carbon.

TABLE 4

Butane–Butadiene Mixtures, v = 1200 liter/liter/hr

Temp., °C	Composition of mixture in mole %		C_4H_8 obtained in % of butane passed	C_4H_8 and C_2H_4 formed on mixture passed in %		Degree of decomposition of C_4H_6 in %
600	82.0	18.0	26.4	5.7	6.2	67.0
620	82.0	18.0	24.9	9.8	9.0	70.3
635	82.0	18.0	23.2	13.7	12.8	74.2

Mixtures of butylene and ethane. Experiments with mixtures containing 50.4 mol. percent of butylene were carried out under the same conditions. It was found that the degree of decomposition of butylene was 50.0% at 600°, 54.5% at 620°, and 59.0% at 635° and about 7% of butadiene was formed, calculated on the butylene passed. The decomposition of butylene was accompanied by the formation of light hydrocarbons (methane, ethane, ethylene, and propylene) and the deposition of carbon on the catalyst, reaching 20% at 600° and 28.9% at 635° (Table 3 and Fig. 1).

Mixtures of butane and butadiene. The mixtures contained 18 mol. % of butadiene. The data obtained are presented in Table 4. The degree of decomposition of butadiene increased with a rise in temperature and when calculated on the butadiene present in the starting mixture it was 67% at 600° and 74.2% at 635°, without allowing for its formation from butane (see Table 1). In addition, the butadiene present in the mixture retarded the dehydrogenation of butane to butylene. The amount of butylene formed, on the butane passed, was only 26.4% at 600° instead of 46.8% obtained by dehydrogenation of pure butane (Table 1).

Mixtures of butadiene and ethane. In order to allow for the decomposition of butadiene, experiments were carried out with mixtures under the same conditions. It was found that over the investigated temperature range of 600-635°, 96-100% of the butadiene was decomposed. The decomposition products of butadiene were light hydrocarbons, tarry materials, and carbon on the catalyst; the latter corresponded to 42-46% of the butadiene decomposed (Table 3 and Fig. 2).

DISCUSSION OF RESULTS

The experiments with mixtures of butylene and butadiene with ethane confirm our previous hypothesis that in the dehydrogenation of butane–butylene mixtures on an aluminum–chromium catalyst the formation of carbon and tarry materials is due to the decomposition of butylene and,to a great extent, butadiene (see Table 3). At 600°, 50% of the butylene is decomposed to form 7.2% of butadiene, 20% of carbon, and about 23% of volatile hydrocarbons. With a rise in temperature to 635°, the degree of decomposition of butylene increases to 59% and this is accompanied by an increase in the deposition of carbon on the catalyst to 28.9% and a decrease in butadiene formation to 6.7% (see Fig. 1). Experiments with mixtures of butadiene and ethane showed that butadiene is cracked more strongly on an aluminum–chromium catalyst than butylene (Table 3). Figure 2 shows that at 600°, 96% of the butadiene is decomposed with the formation of 42% carbon and about 54% of volatile hydrocarbons. At 635°, 100% of the butadiene is decomposed. Experiments with pure butane showed that the maximum yield of butylene (46.7%) is obtained at 600°. With a rise in temperature to 635°, the butylene yield fell to 32.2 mol. percent and this was caused by subsequent decomposition of the butylene.

To determine the relative adsorption coefficients of the reaction products butylene, butadiene, and hydrogen, we measured the dehydrogenation rates of binary mixtures: butane–butylene, butane–butadiene, and butane–hydrogen. The relative adsorption coefficients were calculated from a formula in [2] with allowance for the decomposition of butylene and butadiene on the catalyst, which was determined from data of experiments with binary mixtures with ethane.

The relative adsorption coefficients of butane, butylene, butadiene, and hydrogen at 600° were in the ratio of 1 : 2.6 : 9.0 : 0.95.

The numerical values of the reaction rate constants of butane to butylene and to butadiene and also of butylene to butadiene on an aluminum–chromium catalyst were found by means of the equation for monomolecular catalytic reactions in a flow system [3]. As the dehydrogenation of butane at 600° proceeded to an extent that was not too far from equilibrium, it should be noted that the results obtained are of an approximate nature [4]. The data obtained are presented below:

		K_c, ml · min · ml
Dehydrogenation	1. $C_4H_{10} \rightarrow C_4H_8$	10.9
The same	2. $C_4H_{10} \rightarrow C_4H_6$	0.76
The same	3. $C_4H_8 \rightarrow C_4H_6$	1.9

The ratio of the rate constants of reactions 1 : 2 : 3 = 100 : 7 : 17.4.

The values of the relative adsorption coefficients found and a known formula [5] were used to calculate the change in free energy at 600° for the displacement of butane from the active catalyst surface by butylene and butadiene: $\Delta F_{C_4H_8} = -1662$ cal/mole and $\Delta F_{C_4H_6} = -3815$ cal/mole. The results obtained show that the free energy of adsorption displacement of butane by butadiene is more than twice as great as the free energy of adsorption displacement of butane by butylene.

Thus, in the process examined, i.e., the dehydrogenation of butane–butylene mixtures on an aluminum–chromium catalyst, there are the following reactions: 1) dehydrogenation of butane to butylene, which is retarded by the presence of butylene in the starting mixture; 2) dehydrogenation of butane and butylene to butadiene; 3) decomposition of butane; 4) decomposition of butylene to light hydrocarbons and carbon; 5) decomposition of butadiene to light hydrocarbons, carbon, and condensation products. As a result of the reactions occurring, the dehydrogenation of butane–butylene mixtures on an aluminum–chromium catalyst at atmospheric pressure gives low yields of butadiene on the butane–butylene mixture passed and also on that reacted. The catalyst is rapidly carbonized and requires frequent regeneration. As was shown previously [6, 1], the dehydrogenation of butane to butylene on this catalyst proceeds more selectively and at a lower temperature with the formation of less decomposition products (light hydrocarbons and carbon). This indicates that an aluminum–chromium catalyst is specific for the dehydrogenation of saturated hydrocarbons (butane).

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

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